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A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

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II.

(Continued from Vol. XI, p. 448.)

When ortho-cresol is injected into the jugular vein of a dog in the dose of 0.025 gram to the kilo, dissolved in 30 cc. of glycerin and water, almost convulsive struggles come on followed by staggering, the hind legs being most affected. The animal seems stupid and thrills run through the muscles, but the temperature as taken in the rectum only decreases 3 or 4 tenths of a degree Fahr. Later rapid recovery takes place, the animal running about as usual, in as short a time as twenty minutes. We believe these nervous symptoms to be largely dependent on the cardiac depression produced by the injection of the drug. If as much as 0.066 gram to the kilo is used the symptoms become more marked and saliva dribbles from the mouth, the hind legs being again most affected by the paralysis. No change of moment occurs in the rectal temperature, and in forty minutes the dog seems as well as before the

drug was given. Two hours after the dose the animal recovered entirely and chased a monkey around the room, with no failure of motion whatever.

Given to the frog in the dose of 0.004 gram to the gram, hypodermically into the posterior lymph sac, ortho-cresol causes a loss of reflex action in the hind legs particularly; the muscles and nerves rapidly fail to respond to galvanic stimuli before voluntary movement is lost, and death rapidly occurs from cardiac failure, the heart being found widely dilated and paralysed.

When only 0.0003 gram is placed beneath the skin on the back, in five minutes incoördination and loss of reflex activity come on with relaxation, followed by an increase in reflex activity, which in turn gives way to a decrease, which ends in death. As the primary decrease does not occur to any great extent if the center of Setschenow is cut off, the primary decrease in reflex activity is probably due to stimulation of this center.

Reflexes fail *pari passu* with the failure of electricity to make nerves and muscles respond.

Applied locally to the heart, it causes a white scar on its surface and stops it in diastole.

This compound in the dog produces a tracing of a very extraordinary character (see tracing 1), causing a rapid fall of blood pressure from 124 mm. of mercury to 18 mm. in one minute and a half from the beginning of the injection, when given in the dose of 0.08 gram to the kilo, accompanied by a slowing of the pulse rate from 156 to 102, and finally causing the pen to run along the abscissa line without marking any pulse wave on the drum.

That the fall of pressure is largely vaso-motor is proved by the character of the fall and the fact that asphyxia produces no rise, although if advanced cardiac weakness were present this would be of no value as a test. As the pulse waves immediately before the stoppage were large, but the rate slow, it occurred to us that the arrest might be due to centric inhibitory stimulation, and this was proved to be partly the case by the fact that upon vagal section the heart beat at 90 per minute, the pulse wave returning for a few seconds. That the stoppage is not entirely due to a centric inhibitory action, however, is evident, since this change was immediately followed by arrest only to be once more replaced by a few beats for 20 seconds at the rate of 60 per 60 seconds, the pressure being from 2 to 26 and then 2 to 14 mm. of mercury;

death coming on ten seconds later. In another animal which was curarised and in which the normal arterial pressure was 144 mm. of mercury with a pulse rate at 120 per minute, the dose of 0.033 gram to every kilo caused a fall of pressure amounting to 27 mm. of mercury, and no noteworthy change of pulse rate until three minutes later, when it became much slower, only amounting to 84 per minute, although the pressure at this time had returned to the normal, save that by its range and peculiar scope it seemed to be caused by a heart beat influenced by vagal stimulation. In order to test this point, section of these nerves was immediately made, with the result that the pulse rate became a little faster, but still remained slow, only reaching 90 per minute. It would seem probable, therefore, that two factors are present in the cardiac action of ortho-cresol, viz. cardiac inhibition and depression. Inhibition, because the pulse waves do not show a heart sufficiently paralysed to cause death, and because vagal section sets the heart going for a moment when it is stopped. Depression, because the heart is found relaxed and paralysed after death, and because section of the vagus will not bring on complete cardiac restoration of function. The cardiac depression is also proved by the results obtained by the application of the drug to the heart of the frog. It is worthy of remark that the blood pressure seems to be directly affected by the drug, as well as secondarily influenced by the alterations in cardiac action due to vagal influences, for asphyxia will not cause a rise in pressure.

Meta-cresol given in the dose of 0.05 gram to the kilo of the dog by the jugular vein, well diluted, produces scarcely any noticeable changes save a slight and very fleeting weakening of the muscles which lasts perhaps three or four minutes. The rectal temperature is unaffected, and in a very short time (thirty minutes) the animal is playful and mischievous, entirely well.

When 0.0022 gram to the gram is given to the frog, hypodermically, lassitude, relaxation and partial abolition of reflex action comes on in the hind legs, the fore legs being less affected. The heart is markedly dicrotic and the circulation is poor, as is evinced by venous congestion of the legs and body. Larger doses, 0.044 gram to the gram, cause rapid loss of reflex action and failure of response of muscle and nerve to galvanic stimuli,

before voluntary motion is lost. The heart is at first markedly dicrotic, the venous system is engorged, and the heart finally is stopped in wide diastole. Separation of Setschenow's center from the body does not cause return of reflexes. The hind legs are most affected.

The primary loss of reflex depends on depression of the sensory centers in the spinal cord and sensory nerves followed by depression of the motor cord and the nerves and muscles, as has been proved by finding all these parts lacking in response to galvanic stimuli.

That the paralysing action is profound is proved by the fact that even $\frac{1}{8}$ of a grain of strychnine given hypodermically fails to cause any sign of a convulsion.

Meta-cresol when given by the jugular vein in the dose of 0.09 gram to the kilo, dissolved in 30 cc. of water and glycerin, causes a slight slowing of pulse rate accompanied by a very marked fall of blood pressure, so that while the pulse rate drops from 180 to 150 beats (30 beats), the pressure falls from 140 mm. of mercury to 42 mm. of mercury, and then after the lapse of two minutes reaches 75 mm., the pulse rate has also by this time returned to the rate existing before the drug was given (180). It is to be noted that even when the pressure is lowest the pulse waves are well developed and more full than is common in great cardiac depression. If, while the pressure is at 75 asphyxia be produced, there is no increase of pressure of any extent, and consequently it is fair to assume that the fall of pressure which takes place is due to vaso-motor depression. Six minutes later, the pressure having risen to 122, a second dose of 0.07 gram to the kilo was given, and immediately a second fall of pressure took place with very slight variation in pulse rate. Four minutes after this, the blood pressure having risen once more 105 mm., one gram was given and produced death in thirty seconds by cardiac failure. That the cardiac arrest was not due to inhibitory stimulation is proved by the fact that section of the vagus nerves, immediately, failed to set the heart in action. In another experiment where the dose was 0.15 to the kilogram, death occurred within twenty seconds from the administration of the dose by the jugular vein, there being a fall of pressure almost to the abscissa line, and a gradual failure of cardiac force as shown by the pulse waves. We therefore conclude that meta-cresol acts as a direct depressant poison to the vaso-motor

system, and also to the heart muscle to a less extent, when given in the dose of from 0.05 gram to 0.20 gram to the kilo of the dog's weight, and that it paralyses all vital tissues with which it comes strongly in contact, affecting the sensory nervous system primarily, and the motor system secondarily, paralysing them.

When para-cresol is injected into the jugular vein of a dog not attached to a manometer, but free to run about, and to which no ether has been given in opening the vein, in the dose of 0.1 gram to the kilo in 40 cc. of water and glycerin, marked struggles of a convulsive character come on, amounting finally to a tonic spasm of a moment's duration. Following this is some staggering of gait and evidences of weakness, particularly in the hind legs, lasting for three minutes. As the animal now rapidly recovers, we believe the spasms and subsequent weakness to be due to the circulatory disturbance produced by the drug thrown into the heart *en masse*. There is absolutely no change in the rectal temperature as a result of the use of the drug, and in an hour or so the animal seems as well as ever.

When 0.006 gram to the gram is injected into the posterior lymph sac of a frog, death comes on almost at once, the heart being stopped in diastole. There is response to stimuli in the limbs, which are stiffened almost as with *rigor mortis*.

If 0.002 gram to the gram is given, a few jumps take place as the result of the irritation, reflex action is lost, and incoordination ensues. Crawling takes the place of jumping. Section of the spinal cord to cut off any influences from Setschenow's center fails to restore reflex activity, but later reflexes return and become excessive. The muscles and nerves respond to galvanic stimulus sluggishly. The hind legs seem most affected. The same results, but of a severe character, come on when 0.02 gram is given, the hind legs being merely dragged after the body which is moved by the fore feet, the latter seeming with the nose hyper-sensitive. The muscles and nerves in the hind legs respond poorly to electricity. There is always very marked loss of sensation, due to an action on the receptive side of the spinal cord and also on the sensory nerves. Locally applied to the exposed beating heart it acts as a depressant poison, stopping it very shortly in diastole. From these tests on the dog and frog it would seem proved that

para-cresol acts as a depressant poison to all tissues with which it comes in contact, if in concentrated form, and that while its dominant action is on the circulatory system, it paralyses first the sensory nervous system and then the motor, the posterior parts of the body being most affected.

Para-cresol, when given to a dog by the jugular vein in the dose of 0.08 gram to the kilo, produces immediately a very marked and sudden fall in the blood pressure, with a corresponding decrease in pulse rate. The fall of pressure may amount to nearly 100 mm. of mercury, in from thirty seconds to a minute, and is so sudden as to be very evidently dependent upon cardiac depression and not vaso-motor influence. Immediately after this the pressure rises nearly to the normal as the heart rids itself of the poison. If a second dose be now given a greater fall takes place than before, the pressure equalling only 4 mm. while the pulse also becomes still slower. After the lapse of three minutes from the last dose the pressure partially recovers itself, but the pulse rate remains very much slower than the normal. The pulse waves are also fairly full and stronger than they were immediately after the drug was injected. In order to determine whether the slow rate was inhibitory in its nature the vagus nerves were severed, but the rate and pressure did not increase as they do in the non-poisoned animal under such circumstances. Ten minutes later another dose of 0.04 gram to the kilo produced a fall of pressure and rate followed by a partially compensatory rise of pressure, which, however, immediately fell in death when 0.16 gram to the kilo of the animal's weight was injected in two equally divided doses, twenty seconds apart. The question at once arises as to whether the fall of pulse rate and pressure was entirely due in every instance to cardiac depression, or whether the inhibitory nerves were also stimulated peripherally. This is almost impossible to answer. The cardiac depression was certainly present, and the pneumogastric stimulation peripherally was probably a factor, since other experiments in which smaller doses were used caused cardiac slowing without much cardiac depression; 0.1 gram to the kilo stops the heart in diastolic arrest.

Conclusions.

Ortho-cresol on the heart of the dog and frog acts as a depressant poison. It causes in the frog paralysis of the spinal cord and

sensory and motor nerves, the sensory apparatus being most affected, and diminishes the contractibility of the muscles. It would seem to be a stimulant at first to Setschenow's reflex inhibitory center.

Ortho-cresol produces death by cardiac arrest by depressing this viscus and by stimulating somewhat the centric inhibitory apparatus, when given in the dose of 0.08 gram to the kilo. The depression of the vaso-motor apparatus is also an important factor in producing the fatal issue.

When given in the dose of 0.033 gram to the kilo it slows the pulse by depressing the heart and stimulating the vagus nerves.

Ortho-cresol is, therefore, in small amounts a stimulant to inhibitory nervous protoplasm, and in larger amounts a powerful depressant to all vital tissues.

Meta-cresol has no influence on the inhibitory apparatus of the frog or dog as have ortho- and para-cresol. It is not so powerful a cardiac depressant, but acts more upon the vaso-motor system. On the nervous system it paralyses the sensory and finally the motor apparatus of the body. In the dose of 0,07 to 0.09 gram to the kilo of the dog's weight by the jugular vein it causes cardiac depression, but chiefly acts on the vaso-motor apparatus. When given in as large a dose as 0.15 gram to the kilo by the jugular it produces death by cardiac arrest.

Para-cresol acts upon the frog and dog as a depressant poison to the heart, and secondarily to the nervous system, particularly the sensory apparatus; afterward the nerves and muscles and motor tract of cord are paralysed. In the dog, para-cresol, in the dose of 0.1 gram to the kilo, causes death by cardiac paralysis. In the dose of 0.08 gram to the kilo the pulse becomes slow from a stimulation of the inhibitory apparatus centrically, and perhaps peripherally, accompanied by depression of the cardiac muscle, the vaso-motor system seeming but little if at all affected.

Résumé.

Ortho-, meta- and para-cresol all act as sensory and motor paralysants.

The ortho and para compounds act as stimulants to inhibitory processes; the meta compound has no such influence. The ortho compound seems to be the more powerful inhibitory stimulant of the two, and is the most powerful cardiac depressant of the group.

After ortho-cresol in this respect is para-cresol; meta-cresol having little cardiac influence comparatively; thus, ortho-cresol kills when injected in the strength of 0.08 gram to the kilo, para-cresol in the dose of 0.1 gram to the kilo, and meta-cresol when the amount equals 0.15 gram to the kilo.

Meta-cresol seems to affect the vaso-motor system more than para-cresol, but probably not more than ortho-cresol.

Ortho-cresol and para-cresol are grouped as inhibitory stimulants and cardiac depressants; ortho-cresol and meta-cresol as vaso-motor depressants. On the nervous system of the frog these compounds act as paralysants in the same order as they act upon the heart. Thus of ortho-cresol 0.004 to the kilogram paralyses nerves and causes death. Para-cresol kills at 0.006; meta-cresol only at 0.044 gram to the kilogram.

THE HYDRO-ELECTRIC EFFECT OF STRETCHING METALS.

By C. Barus.

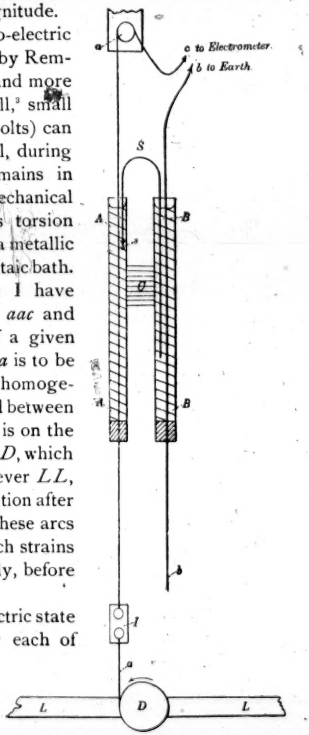
1. The question which forms the subject of the present paper has an important bearing on many problems connected with the viscosity of solids. It is for this reason that I undertook the work.

2. The hydro-electric method is usually conceded to be the most delicate for testing differences of molecular constitution in metals. Hence if a change of molecular structure be among the results of a mechanical strain of any kind imparted to a metal, the change of its electro-positive quality will probably indicate the molecular change. Unfortunately, hydro-electric data are always distorted by polarisation. Polarisation, moreover, is apt to be even larger than the effect to be studied, so that the observer is obliged to resort to methods of measurement in which a fair degree of constancy of the error in question is assured. It follows that unless the hydro-electric effects are as large, for instance, as those produced by temper in steel,[1] the effect of strains which cannot be applied without removing the wire or metal from the hydro-electric

[1] Barus and Strouhal, Am. Jour. Sci. **32**, 276, 1886.

bath is not observable. In such a case the polarisation varies with each immersion in a way quite beyond control. Moreover, certain strains like the drawn strain show different mechanical conditions at different distances from the axis. Hence the hydro-electric constant of such a rod, were it obtainable, would be a complex magnitude.

In magnetisation, the hydro-electric effect of which was discovered by Remsen[1] and studied by Nichols,[2] and more recently by Rowland and Bell,[3] small hydro-electric effects ($<.03$ volts) can be detected because the metal, during straining (magnetisation), remains in place. Among ordinary mechanical strains, traction and perhaps torsion admit of similar application to a metallic wire, left undisturbed in the voltaic bath.



3. In the annexed figure I have shown the apparatus used. *aac* and *bb* are consecutive pieces of a given kind of soft wire. Of these *aa* is to be stretched, *bb* examined in the homogeneous state. Hence *aa* is fixed between two points of which the lower is on the circumference of an iron drum *D*, which can be rotated by aid of the lever *LL*, and is frictionally fixed in position after any arc of rotation. Usually these arcs were 180°, and four or five such strains could be applied consecutively, before rupture ensued.

Measurements of hydro-electric state were made before and after each of these strains. For this purpose both wires were surrounded by a glass tube *AA* and *BB*, respectively, held together by a little block of wood *C*. These tubes were closed

[1] Remsen, this Journal **3**, 157, 1881.
[2] Nichols, Am. Jour. Sci. **31**, 272, 1886; Ibid. **35**, 290, 1888.
[3] Rowland and Bell, Phil. Mag. (5) **26**, 105, 1888.

below with rubber corks, through which the wires passed without leakage. The tubes were filled either with a concentrated solution of zinc sulphate, with distilled water, or with any other liquid which does not act strongly on the metal. The electrolytic connection between AA and BB was made by a siphon S, filled with the liquid of the tubes and closed at s with a parchment septum. The upper ends of the wires b and c were in connection with the terminals of a Mascart electrometer, or with the wires of an apparatus for zero method.

After straining the wire aac to the point of breakage, the apparatus was reversed and bb now strained in the same manner, aac being free. In this way the number of distinct measurements for each adjustment was doubled.

The wire being 54 cm. long and the diameter of the drum about 1.7 cm., the extension of the wire per rotation of 180° was about 2.6 cm., or $\delta L/L = .05$, nearly. The amount differed slightly when wires of different thicknesses were used. The reduction of the diameter of iron wire before and after straining is therefore considerable.

4. The hydro-electric effect of traction is characterised by a temporary and a relatively permanent part. The temporary part may be studied by observing the throw of the needle immediately after straining, as well as the differences of the potential at the end of each of the following minutes. The difference of potential which remains after the temporary effect has subsided I called the permanent part. An allowance of five minutes was usually regarded sufficient. This assumption is somewhat arbitrary; but the errors committed are of like effect throughout the series. The value of the throw is expressed in volts (as are the other electrical data), and is given as an *increment*, that is, without reference to the actual potential of the stretched wire. It is to be noticed, moreover, that the temporary effects are measured *without* commutation. The permanent effects are measured with commutation, each wire being alternately put to earth, while the other is connected with the electrometer (Mascart's key). I made about seven series of the following kind, two of which are given in Table I. The diameter of the wire before straining was $2\rho_a = .086$ cm.; after straining $2\rho_b = .078$ cm.

TABLE I.—*Hydro-electric Effect of Stretching Iron Wire.*

Strain.	Throw $e\times10^3$ temporary.	$e\times10^3$ permanent.	Strain.	Throw $e\times10^3$ temporary.	$e\times10^3$ permanent.
O	...	+ 9	O	...	+ O
I	−34	+ 7	I	−18	+ 5
II	− O	+11	II	− 2	+ 9
III	+ 8	+14	III	+ 5	+11
IV	...	...	IV	+10	+13
O	...	−14	O	...	− 6
I	−26	−13	I	−15	− 1
II	− O	− 8	II	− O	− O
III	+10	− 4	III	+ 2	+ 2
IV	+12	− 1	IV	+ 5	+ 3

Extension, $\delta L/L = .05$ per pull. Radial contraction, $\delta\rho/\rho = .022$ per pull. Mean permanent potential increase $= +.003$ volts per pull.

The table shows that the permanent effect is distinctly electro-positive; negative differences are numerically decreased, positive differences are increased. The increase of electro-positive quality takes place simultaneously with the increase of length, at a rate which varies somewhat in different experiments, but the mean value of which is about .003 volts per extension $\delta L/L = .05$. This is equivalent to a decrease of the wetted external surface of the wire, of about 5 per cent., supposing there is no change in the specific volume of the metal. The measured value is less than this, for the circumference before straining was found to be $2\pi\rho_s = .27$ cm., after straining (aggregate of the four pulls) $2\pi\rho_h = .24$ cm. This is less than 3 per cent. of the wetted surface, per pull.

The temporary effect is equally definite in character. Apart from the value of the permanent effect, the former is at first negative, which (negative) quality is then successively reduced, until by passing through zero it becomes positive. The intensity of the first negative throw is, as a rule, stronger than the final positive throw.

5. It is expedient to indicate in passing some probable cause for the phenomena. Iron submerged in an aqueous solution is polarised positively and covered with a coating of hydrogen. Hence it is practically a condenser, whose capacity increases directly with the wetted surface, *caet. par.* The effect of strain is therefore twofold in kind. If in consequence of the jarring or vibration which unavoidably accompanies stretching, some of the gas is mechanically skaken off, the positive polarisation is decreased.

This is probably indicated by the negative throw of the needle, immediately after the first strain. Simultaneously with this result the capacity of the wire is diminished, in consequence of stretching (wetted surface decreased). Hence the positive polarisation or potential is again increased. If the last effect gradually predominates over the other (effect of jar), the temporary throw changes from negative to positive. This explanation is the nearest at hand and it need not be sufficient; but it is clear at once, that before any hydro-electric change can be ascribed to strain as such, it is necessary to evaluate the polarisation error, as well as other minor errors, such for instance as are due to the increase of the temperature of the wire due to stretching. Cf. Wiedemann's "Elektricität," Vol. II, p. 773, etc.

6. In the following tables I have inserted data corresponding to Table I, but obtained in the same way with German silver, brass, copper and iron, all the wires being of larger diameter than above. The notation is that already used. In Tables II to V a concentrated solution of zinc sulphate is the electrolyte; in the other cases distilled water is used. At the ends of the tables the mean value per pull of the extension, $\delta L/L$, the radial contraction, $\delta\rho/\rho$, and the permanent increase of potential, e volts, are inserted for each wire.

TABLE II.

German silver $\begin{cases} 2\rho_a = .102 \text{ cm.} \\ 2\rho_h = .093 \text{ cm.} \end{cases}$

Zinc sulphate.

Strain.	$\times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$e \times 10^3$ permanent.
0	...	...	...	...	...	+27
I	+36	12	12	13	16	+28
II	+42	16	6	− 4	−19	+35
III	+50	19	− 1	−10	−18	+47
IV	+69	42	18	9	2	+51
0	...	...	...	..	...	+24
I	+32	13	7	4	4	+30
II	...	...	...	...	...	+26
III	...	...	...	...	...	+24
IV	...	...	...	...	...	+23
V	...	...	...	...	...	+18

Extension per pull, $\delta L/L = .05$.

Radial contraction per pull, $\delta\rho/\rho = .022$.

Mean permanent potential increase per pull $= .005$.

TABLE III.

Brass $\begin{cases} 2\rho_s = .166 \text{ cm.} \\ 2\rho_h = .157 \text{ cm.} \end{cases}$

Strain.	$\epsilon \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$\epsilon \times 10^3$ permanent.
0	...	...	...	...	...	+23
I	+21	18	12	12	13	+39
II	+41	31	28	25	24	+59
III	+48	30	20	18	15	+65
IV	...	...	...	...	...	...
0	...	...	...	...	...	−15
I	+17	4	2	0	− 2	−18
II	+18	10	6	3	1	−18

Extension, $\delta L/L = .05$ per pull.
Radial contraction, $\delta\rho/\rho = .013$ per pull.
Mean permanent potential increase per pull $= .015$.

TABLE IV.

Copper, $2\rho_s = .166$ cm.
Zinc sulphate, $2\rho_h = .150$ cm.

Strain.	$\epsilon \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$\epsilon \times 10^3$ permanent.
0	...	...	...	...	...	+4
I	0	0	0	0	0	+6
II	0	0	0	0	0	+6
III	+3	2	1	2	2	+6
IV	2	2	...	...	...	...
0	...	...	...	...	...	−6
I, II	+2	2	2	2	2	±0
III, IV	+2	2	2	...	...	−1

Extension per pull, .05.
Radial contraction per pull, .024.
Mean permanent potential increase per pull, .001.

TABLE V.

Iron, $2\rho_s = .156$ cm.
Zinc sulphate, $2\rho_h = .147$ cm.

Strain.	$e \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$e \times 10^3$. permanent.
0	...	...	...	...	...	+8
I	−58	−42	−29	−22	−17	−6
II	−36	−24	−12	− 1	− 5	−5
III	−22	− 3	− 2	− 2	− 1	−3
IV	−36	−24	−17	−14	−10	−7
0	...	...	...	...	...	+4
I	−52	−38	−24	−18	−15	−7
II	−30	−17	−10	− 6	− 4	−7
III	−30	−18	− 6	− 4	− 0	−7

Extension per pull, .05.
Radial contraction per pull, .014.
Mean permanent potential increase per pull, −.003.

TABLE VI.

Brass, $2\rho_s = .166$ cm.
Water, $2\rho_h = .154$ cm.

Strain.	$e \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$e \times 10^3$ permanent.
0	...	...	...	...	...	−76
I	+82	73	59	48	39	−44
II	+58	40	22	8	−2	−52
III	+63	49	28	14	7	−56
IV	+62	44	27	14	8	−60
0	...	...	...	...	...	+ 73
I	+42	42	42	38	36	+103
II	+21	14	13	8	6	+ 91
III	+28	21	11	−1	0	+ 77
IV	+29	24	14	7	3	+ 67

Extension per pull, .05.
Radial contraction per pull, .018.
Mean permanent potential increase per pull, ±.015

TABLE VII.

Iron, $2\rho_s = .135$ cm.
Water, $2\rho_h = .126$ cm.

Strain.	$\epsilon \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$\epsilon \times 10^3$. permanent
0	...	...	...	...	...	+16
I	−17	+46	60	67	70	+79
II	−10	+24	28	29	...	+95
0	...	...	...	...	...	−56
I	−33	−17	− 6	−3	−1	−40
II	− 4	+ 7	+14	...	...	−23
III	− 6	+13	+14	...	...	− 6

Extension per pull, .05.
Radial contraction per pull, ——
Mean permanent potential increase per pull, +.027.

TABLE VIII.—*Promiscuous Work.*

Copper wire. Distilled water.

Strain.	$\epsilon \times 10^3$ temporary. Throw.	1m.	2m.	3m.	4m.	$\epsilon \times 10^3$ permanent.
0	...	...	...	...	..	+15
Jerk	−42	+ 2	...	...	...	+ 4
Jerk	−35	− 4	...	...	...	+ 2
I, II	+29	+28	+29	+34	...	+27
III, IV	+13	+ 9	+ 7	+ 8	...	+28

Extension per pull, .05.
Radial contraction per pull, .024.
Potential increase per pull, .015.

Iron wire. Distilled water.

0	...	...	...	...	...	−40
Jerk	−42	−15	−6	+2	...	−39
Jerk	−49	−28	−6	+1	...	−36
Jerk	−45	−21	−7	...	...	−36
After long waiting						−18

		Brass wire.		Distilled water.		
o	...	...	...	...	...	— 8
Jerk	—21	...	...	...	...	—25
Jerk	—35	...	...	..	...	—29
Jerk	—17	...	...	...	...	—21
Rub	...	...	...	...	...	—10
Rub	no temporary effect					— 6
Rub						— 9
o	...	...	...	...	...	— 6
I	+35	35	35	31	31	+25

German silver $2\rho = .08$ cm.; zinc sulphate.

Strain.	$e \times 10^3$ permanent.	Strain.	$e \times 10^3$ permanent.
o	+13	o	—1
I	+ 7	I	—6
II	+ o	II	—6
III	— 6	III	—6

7. Turning first to the permanent hydro-electric effect of traction, Tables II and III show increments of decidedly larger positive value than hold for iron in Table I. The effect for copper in Table IV is nearly zero, and for iron in Table V actually negative. Whatever the effect may be, it must necessarily be considered doubly specific, depending both on the metal and the liquid. Hence I made further investigations in Tables VI, VII and VIII by replacing the zinc sulphate solution by water. Thus it is found that the permanent effect is decidedly greater in magnitude for water than for zinc sulphate, from which the close relation of these phenomena and polarisation may be inferred. The effect in the case of water, moreover, is by no means as regular as in the other case. In Table VI, for instance, the permanent points enclose a figure of rhomboidal outline, showing that the effects of initial pulls are different from the final pulls. Again, copper which in zinc sulphate is not changed hydro-electrically by traction, in water shows effects quite comparable to the other metals. Iron-water data are excessively large. Irrespective of sign, the hydro-electric effect increased with the diameter of wire used.

Among results bearing on section 9 below, I may mention that the permanent effect of traction of iron in zinc sulphate is sometimes positive, sometimes negative, depending on the qualities of

the wire. Table VIII shows a specimen of German silver in which the permanent effect is negative.

I have given the temporary effects in their absolute value (increments) aside from the diameter of the wire. In case of German silver, of brass, of copper, these effects are distinctly positive (opposite in sign to the first iron effects).

Returning to the explanation suggested in section 5, it appears that in German silver, copper and brass the effect of diminished capacity and of exposure of fresh surface[1] due to stretching, both of which are positive, predominate over the negative effect of incidental jerking. In iron, since the temporary effect is first negative, they do not so predominate. It is specially to be noticed that the permanent effect is entirely independent of the temporary effect. Inasmuch as the permanent effect is obtained by commutation (each electrode being alternately put to earth), the residuum of the temporary effect is discharged. From this it might be conjectured that the apparatus acts like a doubled condenser.

In Table VIII, I give some data bearing on the probability of this explanation. The wires were adjusted in the usual way; but instead of being stretched, were only jerked by the action of the machine. In this case a negative temporary effect is obtained in *all* the metals, about of the same numerical order as the data in the earlier tables. Similar results follow after rubbing the immersed parts of the wires.

It might be inferred that the temporary effect is due to friction at the axle of the drum. But I found in special experiments that all such charge escapes to the earth without influencing the electrometer.

8. Since the immersed part of the wire is of the form of a cylinder of length l and radius r, its capacity is approximately

$$C = l/2 \ln \frac{1}{r}.$$

If the charges are constant, so that $Q = VC = V'C'$, or $V/V' = \log r/\log r'$, it follows that (V_1' and V being identical)

$$V_1' = \frac{\log r'}{\log r - \log r'}(V - V'). \qquad (1)$$

[1] This being at once acted on by the liquid, falls under the considerations made in the text above.

From this expression the polarisation of the wire may be calculated, when the difference of potential due to traction is known. The data of Tables I to VIII then furnish the following values of V_1'. The subscripts attached to the symbols of the metals refer to the number of the table from which the data are taken.

Metal.	Fe_1	G. $S._2$	$Brass_3$	Cu_4	Fe_5	Br_6	Fe_7	Cu_8
$\log r/\log r/r'$	26	26	33	19	32	25	30	19
$\Delta V \times 10^8$	4×3	4×5	4×15	4×1	-4×3	$\pm4\times15$	4×27	4×15
V_1'	$+.31$	$+.52$	$+1.98$	$+.08$	$-.38$	±1.50	$+3.24$	$+1.14$
			$ZnSO_4$				H_2O	

If the wire and its surrounding liquid be regarded a condenser, of which the film of gas (hydrogen) is the medium through which induction takes place, the capacity is

$$C=\frac{r_1 lk}{e}\left(1+\frac{e}{2r_1}\right), \text{ nearly,}$$

where e is the thickness of the film of gas, r_1 the radius of the wire, the specific inductive capacity being $k=1$. If then the charge be regarded constant as before, an equation similar to (1) may be obtained by introducing some reasonable postulate relative to the thickness e. Suppose e is constant, i. e. before and after pulling the layer of gas is not changed in thickness. Then the potential V_2' of the immersed wire is

$$V_2'=\frac{r}{r'-r}(V-V'). \qquad (2)$$

Again, suppose the mass of the film of gas to be constant, so that $2\pi re=2\pi r'e'$. Then the potential of the immersed wire is

$$V_3'=\frac{r^2}{r'^2-r^2}(V-V') \qquad (3)$$

On this assumption Tables I to VIII furnish the following digest:

Metal.	Fe_1	G. $S._2$	$Brass_3$	Cu_4	Fe_5	$Brass_6$	Fe_7	Cu_8
V_2'	.12	.21	1.06	.04	—.20	$\pm$ .76	1.54	.57
V_3'	.22	.38	2.04	.07	—.38	$\pm$1.50	3.00	1.08

In discriminating[1] between the values V_1, V_2, V_3, it is clear that

[1] The close analogy of a polarised voltameter and a double condenser was pointed out by Varley (Phil. Trans. **161**, 129, 1872), and investigated by Colley (Wied. Ann. **7**, 206, 1879) and others. The subject is minutely discussed in Wiedemann's Elektricität **2**, 758–771. It may be observed that in equation (2) the increment of potential varies as the decrement of wetted surface.

the conditions of V_1 are not given, and that the maximum probability rests with V_2; but this quantity is not decidedly above the order of possible polarisation for the cases under discussion. Hence the permanent hydro-electric effect due to a change in the electro-positive quality of a metal by traction is obscured beyond recognition by the unavoidable variations of polarisation which accompany the experiment.

Having thus failed to obtain reliable evidence from hydro-electric experiments, I endeavored with some pains to discern a direct electrical effect (potential) due to the traction of a single insulated wire immersed in an electrolyte. These experiments may be omitted here; they contribute no essentially new data. So far as my work went, no certain permanent indication of a hydro-electric effect of strain could be obtained by any of the methods applied.

9. In the above paragraphs I have endeavored to refer the very definite hydro-electric results obtained to the simplest explanation at hand. But it is necessary to bear in mind that the phenomena are so largely beyond the observer's control that an exhaustive experimental discussion is out of the question. It would be unwise, therefore, to lose sight of other points of view from which they may have a direct bearing on the real question in hand, viz. the possibility of molecular change in a metal, corresponding to each change of strain imparted to it. The question is steadily gaining in probability. Osmond, after making an elaborate pyrometric study of the conditions under which Gore's phenomenon occurs in iron, postulates the existence of an α and a β variety of iron. These varieties when cold may be distinguished physically by their difference in hardness. Moreover, β-iron, besides being produced spontaneously out of α-iron, above a certain temperature in red heat, may also be produced in small quantity by straining α-iron at ordinary temperatures. I pointed out that such an hypothesis involves the occurrence of α and β varieties of most metals, even when no such criterion as is given by Gore's phenomenon is observable. Quite recently Mr. Carus-Wilson,[1] from experiments made on the viscosity of strained steel, summarises his experience in favor of Osmond's[2]

[1] Carus-Wilson, Nature **41**, 213, 1890.

[2] Osmond, Annales des Mines, July–August, 1888; Mém. de l'artillerie de la Marine, Paris, 1888, p. 4.

view. Unfortunately, the well known effects of strain on the thermo-electric quality and on the resistance of metals are not at once interpretable, except perhaps in so far as they are accompanied by hysteresis (Cohn, Warburg, Ewing, Schumann). The ion theories of metallic electrical conduction now coming into vogue (J. J. Thomson, Giese[1]), conditioned as they must be by the occurrence of marked molecular instability in metals, are steps in the same direction. I will therefore merely point out, in concluding, that the simple explanations given above for the temporary effect, which was found consistently negative at first in iron, and consistently positive in all the other metals, is not satisfactory. It is permissible to regard it as the direct result of a change of molecule due to straining; for it is precisely in the first stages of the temporary effect that evidence for such molecular change may reasonably be sought.[2]

Contributions from the Chemical Laboratory of Harvard College.

LXVII.—ON THE ACTION OF SODIUM ACETACETIC ESTER UPON TRIBROMDINITROBENZOL.

By C. Loring Jackson and George Dunning Moore.[3]

After the action of sodium malonic ester on tribromtrinitrobenzol and on tribromdinitrobenzol had been studied, it seemed of interest to determine whether sodium acetacetic ester acted in the same way, and the following paper contains the results of experiments undertaken with this intention upon the tribromdinitrobenzol, which was selected because it can be prepared so much more easily than the corresponding trinitro compound. These results can be sum-

[1] Giese, Wied. Ann. **37**, 576, 1889.

[2] Cf. Rowland and Bell (*l. c.*), who are obliged to base their inferences on the temporary hydro-electric effect of magnetisation. In all problems of this character it is necessary to distinguish between the positional stability and the chemical stability of a molecule. It does not follow that if the former quality is increased, the latter will also be, for a chemical solvent does not pick up molecules bodily, but by disintegrating them. In certain experiments on the isothermal electromotive force of a Daniell between 10 and 1800 atmospheres, I will indicate this further.

[3] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

marised briefly as follows. Tribromdinitrobenzol behaves with sodium acetacetic ester in the same way that it does with sodium malonic ester: that is, one atom of its bromine is replaced by the acetacetic radical

$$CH_3COCHCOOC_2H_5,$$

and a second by hydrogen, while the third remains unaltered; so that the product of the action is the bromdinitrophenylacetacetic ester,

$$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5,$$

or to speak more accurately its sodium salt,

$$C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5.$$

The bromdinitrophenylacetacetic ester melts at 96°, and possesses marked acid properties, forming the sodium salt whose formula has just been given, even with acid sodic carbonate in aqueous solution. The salt has a red color and is soluble in water; in fact, it resembles the sodium salt of the corresponding malonic compound most closely.

The bromdinitrophenylacetacetic ester is saponified and decomposed by heating with sulphuric acid of specific gravity 1.44, giving the bromdinitrobenzylmethylketone,

$$C_6H_2Br(NO_2)_2CH_2COCH_3,$$

but no trace of the corresponding acetic acid. This ketone melts at 112°–113°, and also possesses acid properties, giving a purplish red salt soluble in alcohol, but decomposed almost completely by water. The acid properties of the ketone are less marked than those of the acetacetic ester, as was to be expected, since the hydrogen, which is replaced by basic radicals, is subject to the influence of an acetyl, a carboxylester and a dinitro phenyl group in the acetacetic compound, only to those of an acetyl and a dinitro phenyl group in the ketone.

The bromine of the ketone can be replaced easily by the aniline radical C_6H_5NH, forming anilidodinitrobenzylmethylketone,

$$C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3,$$

which melts at 131°, and has not lost all acid properties, although they have been much weakened by replacing the bromine atom by the basic radical C_6H_5NH. It cannot form an ammonium salt, but

the sodium salt can be easily obtained in alcoholic solution, and on analysis gave a number corresponding to the formula

$$C_6H_3(C_6H_5NH)(NO_2)_2CHNaCOCH_3.$$

It is completely decomposed by water, but dissolves in alcohol with a brown color.

Both these ketones, therefore, show stronger acid properties than desoxybenzoine $C_6H_5COCH_2C_6H_5$, the metallic compounds of which, according to Victor Meyer,[1] could not be isolated; we are inclined to ascribe this to the presence of the nitro groups in the phenyl, which would heighten its acid-producing power, but it may also be due in part to the fact that these ketones contain the acetyl group, which, as Claisen and Ehrhardt[2] have pointed out, has a greater influence in producing acidity than the benzoyl radical contained in desoxybenzoine.

The hydrazone of the anilidodinitrobenzylmethylketone,

$$C_6H_3(C_6H_5NH)(NO_2)_2CH_2C(NNHC_6H_5)CH_3,$$

was also prepared, and melted at 140°.

The full details of the work will be found in the remainder of the paper.

Preparation of Tribromdinitrobenzol.

The method used by us for preparing tribromdinitrobenzol differs from that formerly in use only in certain details, but, as careful attention to these details insures a purer product at much less expense of time and labor, we have thought it best to give a full account of our mode of procedure.

To make the tribromaniline, 60 grams of aniline were dissolved in dilute hydrochloric acid, and, the solution having been made up to a volume of about 3 liters, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, and washed with a stream of common water until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of the tribromaniline was obtained, and it was free from colored by-products.

[1] Ber. d. chem. Ges. **21**, 1291 (1888).

[2] Ber. d. chem. Ges. **22**, 1019 (1889).

In order to convert the tribromaniline into tribrombenzol, 50 grams of it, after being pulverised, were dissolved with the aid of heat in about 300 cc. of common alcohol, and a concentrated aqueous solution of 21 grams of sodic nitrite poured in slowly, but not in successive portions. The hot mixture was then acidified with dilute sulphuric acid, and allowed to stand over night, when it was filtered, and the precipitate washed with hot water to remove the sodic sulphate and leave the tribrombenzol. An additional quantity of this was obtained by concentrating the alcoholic filtrate, when it separated as an oil, that solidified on standing, and was then crystallised from alcohol. The yield was nearly quantitative, as 45.50 grams of tribrombenzol were obtained instead of the 47.77 required by the theory, that is 95 per cent. When made by this method, the tribrombenzol was usually pure enough to be nitrired directly in spite of its brownish color.[1]

To convert the tribrombenzol into the dinitro compound, 25 grams of it were added to 100–120 grams of nitric acid[2] of specific gravity 1.52 (made from potassic nitrate and sulphuric acid in the laboratory), warmed gently until the solid had dissolved, and allowed to stand about two hours, when the tribromdinitrobenzol crystallised out in large white prisms. The yield was essentially quantitative.

Bromdinitrophenylacetacetic Ester,
$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5$.

Preparation.—This substance was made by the action of an alcoholic solution of sodium acetacetic ester on a benzol solution of the tribromdinitrobenzol in the proportion of about four molecules of the former to one of the latter. For this purpose 15 grams of tribromdinitrobenzol were dissolved in about 150 cc. of benzol, and mixed with 20 grams of acetacetic ester previously treated with 3 grams of sodium dissolved in about 150 cc. of absolute

[1] The amount of sodic nitrite used in the process described above (two molecules of nitrite to one of the base) is twice that required by the theory, but we have found that this large excess was necessary to bring all the tribromaniline into the reaction. When a smaller amount of nitrite was used, the product was much less pure, as shown by its lower melting point; it was necessary in this case to distil it from a little retort, and crystallise several times from alcohol, to obtain pure tribrombenzol. The crystals obtained on evaporating the alcoholic mother liquors, which made up about two-thirds of the entire amount, were distilled with steam, pushing the distillation as rapidly as possible, when tribrombenzol passed over, and tribromaniline was left in the retort; but all this tedious purification can be avoided by using the excess of nitrite recommended above.

[2] This Journal **9**, 350 (1887).

alcohol. At first there was very little change of color, but on standing at ordinary temperatures the liquid turned first yellow and then red (whereas with malonic ester the red color appeared instantaneously). In order to complete the reaction, the mixture was heated on the steam-bath for about one hour, at the end of which time it had become nearly black, and a considerable precipitate of sodic bromide had formed. It was then mixed with from one and a half to two liters of water, and the reddish benzol solution, which was precipitated, removed from the dark red aqueous liquid; the latter was then acidified with dilute sulphuric acid, taking care to avoid a large excess; this decomposed the red sodium salt of the new substance, which was set free in the form of a yellowish oil, and extracted by shaking the liquid with ether twice. On distilling off the ether a dark reddish brown oil was left, which, when cold, was treated with very little alcohol, and upon stirring became filled with crystals, the quantity of which increased on standing for twelve or more hours. When the quantity of the crystals did not increase further, the pasty mass was sucked out on the pump, first adding a little alcohol, if necessary, and by washing with a small quantity of cold alcohol all the very soluble red oil was removed from the crystals, which were nearly or quite insoluble in cold alcohol, and were next purified by crystallisation from hot alcohol until they showed the constant melting point 96°. An additional quantity of the substance can be obtained from the benzol solution by distilling off the benzol and treating the residue with sodic hydrate and a little alcohol, which convert the new substance into its sodium salt, and this can be removed from the unaltered tribromdinitrobenzol by washing with water; when the wash-waters were acidified, and the precipitate purified in the same way as the main portion, the substance was dried *in vacuo*, and analysed with the following results:

I. 0.2683 gram of the substance gave on combustion 0.3788 gram of carbonic dioxide, and 0.0748 gram of water.

II. 0.2512 gram of the substance gave 16.7 cc. of nitrogen at a temperature of 22° and a pressure of 759.7 mm.

III. 0.2067 gram of the substance gave, according to the method of Carius, 0.1041 gram of argentic bromide.

IV. 0.2141 gram of the substance gave 0.1059 gram of argentic bromide.

	Calculated for $C_8H_4Br(NO_2)_2CH_2COCHCO_2C_2H_5$.	Found. I.	II.	III.	IV.
Carbon	38.41	38.50	...	...	...
Hydrogen	2.93	3.09	...	...	...
Nitrogen	7.47	...	7.33	...	...
Bromine	21.33	...	...	21.43	21.05

The yield of bromdinitrophenylacetacetic ester, prepared by the method described above, is satisfactory on the whole, the best result being as follows:

15 grams of the tribromdinitrobenzol yielded 6.5 grams of the ester, and 3.1 grams of unaltered tribromdinitrobenzol were recovered, leaving 11.9 grams which had entered into the reaction. 11.9 grams of tribromdinitrobenzol should yield 11.0 grams of bromdinitrophenylacetacetic ester. The actual yield, therefore, was 59 per cent. of the theoretical. In other preparations the yield varied from 54 to 34 per cent., the lowest which was obtained from this process. The yield was not improved by increasing or by diminishing the proportion of acetacetic ester to the tribromdinitrobenzol. In our first preparations the reaction was allowed to run in the cold, as an experiment, in which the mixture had been heated less than one hour, seemed to give a very unmanageable product; in this case, however, the yield was very much less than that obtained by the process described above, in which the mixture was heated one hour.

In order to throw light on the way in which the reaction runs, we determined the amount of bromide of sodium formed in two preparations as follows:

I. 12 grams of tribromdinitrobenzol yielded 4.43 grams of bromine in the form of sodic bromide.

II. 12 grams of tribromdinitrobenzol yielded 4.40 grams of bromine in the form of sodic bromide.

If two atoms of bromine are removed from each molecule by this reaction, 12 grams of tribromdinitrobenzol would lose 4.74 grams of bromine.

Percentage of bromine removed as sodic bromide,—

I.	II.
93.5	93.0

From this it appears that all the bromine removed from the tribromdinitrobenzol is finally in the state of sodic bromide, as the slight loss of 7 to 6.5 per cent. is not greater than would be

expected when it is considered that the aqueous solution containing the sodic bromide was shaken out twice with ether. These determinations show also that in these cases the whole of the tribromdinitrobenzol entered into the reaction, and, in fact, none of it could be found unaltered in the products of these two preparations; but this was not always the case, as, for instance, in the preparation described on page 169.

The full explanation of the reaction, however, was to be found in the study of its secondary product, the red oil removed from the crystals by washing with cold alcohol. This, upon long standing exposed to the air, threw down a few more crystals of bromdinitrophenylacetacetic ester, which would raise the yield a little above that given, but the amount obtained in this way was very small. The oil, after no more crystals could be obtained from it, was distilled under diminished pressure and yielded some acetacetic ester, leaving in the flask a tarry mass which has shown no signs of giving crystals even after long standing. This part of the work therefore was not carried further, as from the formula of the ester and the removal of all the bromine as sodic bromide there can be no doubt that the reaction with acetacetic ester runs in the same way as that with malonic ester, and in this latter case the reaction has been fully explained.[1] Reasoning on this analogy, the following reactions may be taken as expressing what takes place in the formation of the bromdinitrophenylacetacetic ester.

$$C_6HBr_3(NO_2)_2 + 2\,CH_3COCHNaCOOC_2H_5 =$$
$$C_6HBr_2(NO_2)_2CH_3COCHCOOC_2H_5 + NaBr$$
$$+ CH_3COCHNaCOOC_2H_5 =$$
$$C_6HBr_2(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCH_2COOC_2H_5$$
$$+ NaBr =$$
$$C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCHBrCOOC_2H_5$$
$$+ NaBr.$$

The bromacetacetic ester being afterward attacked either by a molecule of sodium acetacetic ester or by sodic hydrate.

The only question with regard to these reactions, which might arise, would be due to the fact that only a little over 50 per cent. (59 per cent.) of the ester was obtained, which might lead to the hypothesis that nearly half of the tribromdinitrobenzol went to form another substance; but this objection is removed by the fact

[1] This Journal **12**, 15 (1890).

that in another analogous case as much as 80 per cent. of a corresponding ester has been found. We consider, therefore, that the missing 41 per cent. of the ester remained dissolved in the oily secondary product, but should state, on the other hand, that upon treating the oil with sulphuric acid of specific gravity 1.44 in hopes of decomposing the secondary products and converting the bromdinitrophenylacetacetic ester into bromdinitrobenzylmethylketone, we obtained nothing but black tarry substances, from which no substance fit for analysis could be obtained.

Properties.—The bromdinitrophenylacetacetic ester crystallises well, usually in forms looking like a rhombohedron with a very acute angle, less frequently in prismatic forms, which are twinned on a central line parallel to their longer axis, the termination being in shape either like a simple gable, or one with a notch in its point. The crystals show a great tendency to twin, or group, often in forms like those of frost, and are sometimes from 2 to 3 mm. long. The substance has a yellow color of about the shade of potassic chromate, which is characteristic, as the corresponding malonic compound is nearly white. Heckmann[1] has observed a similar deep yellow color in the orthoparadinitrophenylacetacetic ester. It melts at 96°; is very slightly soluble in water, rather more so in hot than in cold; essentially insoluble in ligroine; not very soluble in cold alcohol, but freely in hot; if anything less soluble in methyl than in common alcohol both cold and hot, but the solubility is much greater in the hot methyl alcohol than in the same solvent when cold; tolerably soluble in carbonic disulphide, or ether; soluble in glacial acetic acid; and freely in benzol, chloroform, or acetone; from ether, benzol, or chloroform it is deposited as an oil. The best solvent for it is hot alcohol. Strong sulphuric acid does not act upon it in the cold, but when warm dissolves it, forming a slightly yellowish solution. Strong hydrochloric acid has no action with it in open vessels, even if heated. The decomposition of the substance by these two acids under proper conditions is described later in this paper. Strong nitric acid has no action on it in the cold, but dissolves it when warm; there is, however, no marked change of color, in which respect this substance shows a striking difference from the bromtrinitrophenylmalonic ester, but resembles the bromdinitrophenylmalonic ester.

The bromdinitrophenylacetacetic ester shows marked acid

[1] Ann. Chem. (Liebig), **220**, 133.

properties, as was to be expected from the position of one of its hydrogen atoms upon a carbon adjacent to an acetyl, a carboxyl-ester, and a phenyl group, the latter rendered still more efficient by the presence of two nitro groups, and also from the acid properties of the corresponding malonic compound. Aqueous sodic or ammonic hydrate dissolves it, forming a red solution of the corresponding salt; an aqueous solution of potassic carbonate acts upon it in the same way, giving, however, a somewhat fainter color, but, if alcohol is added to the solution, it turns at once dark red; acid sodic carbonate in aqueous solution gives a very faint red color, which is much intensified by addition of alcohol to the solution. The red solution of the ester in ammonic hydrate is decomposed by heating, or even by exposure to the air at ordinary temperatures, and we were not able to obtain a solution which did not smell of ammonia, even when a large excess of the ester was used; it is evident, therefore, that its ammonium salt is very unstable. We have, however, tried the action of a solution prepared from an excess of the ester and ammonic hydrate with various reagents, and found the following characteristic reactions.

Magnesium or Calcium salt, heavy flocculent precipitate of the color of chrome yellow.

Strontium salt, a less heavy precipitate of a redder color.

Barium salt, a still smaller precipitate, also reddish.

Zinc salt, a pale yellow precipitate.

Cupric salt, a pale yellow precipitate.

Lead salt, a dark yellow precipitate.

Silver salt, a yellowish white precipitate.

The most striking thing about these salts is that the calcium salt is less soluble than that of strontium, and this less soluble than the barium salt. Bischoff[1] has observed a similar peculiarity in the salts of orthonitrobenzoylmalonic ester, and we have found it in the salts of bromtrinitrophenylmalonic ester.

With aniline the bromdinitrophenylacetacetic ester gave only a waxy yellow mass, from which there seemed little chance of obtaining a substance in a state fit for analysis. We have, therefore, abandoned the further study of this reaction, in which undoubtedly the aniline acted on the acetacetic ester radical as well as on the bromine in the benzol ring. That this bromine had been removed we proved by detecting aniline bromide among the products of the reaction.

[1] Ann. Chem. (Liebig) **251**, 362.

Sodium Salt, $C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5$.

In the earlier portions of our work on the bromdinitrophenylacetacetic ester and allied bodies the determination of the composition of the salts was of the greatest importance, as this was the only experimental method which we had found for deciding between the formulas,

I. $C_6H_2Br(NO_2)_2CH_2COCHCOOC_2H_5$,
II. $C_6HBr(NO_2)_2CH_3COCCOOC_2H_5$.

This, at present, is no longer the case, as the discovery of acetylentetracarbonic ester or tartronic acid as a secondary product in the formation of the corresponding malonic compounds can be explained only if a formula similar to I is adopted, and the easy conversion of bromdi- (or tri-) nitrophenylmalonic ester into the corresponding toluol compound also could hardly be brought into harmony with a formula like II. No similar proof has been applied to the acetacetic compound, it is true; but when the close resemblance between this and the malonic compounds is considered, there can be no doubt that they are similarly constituted. The composition of the sodium salt therefore becomes of secondary importance, and this is fortunate, as we have not succeeded in preparing it in a state of purity sufficient to decide between the salts derived from formulas I and II, although our analyses leave no doubt as to its composition, if the first formula is adopted as correct.

The salt was prepared by adding to a solution of the bromdinitrophenylacetacetic ester in absolute alcohol a solution of sodic hydrate or ethylate also in absolute alcohol, taking care that the ester was in decided excess. The deep red alcoholic solution thus obtained was evaporated rapidly to dryness in a narrow beaker sunk throughout its whole height in a water-bath, some ether having been added previously in order that its vapor might protect the solution from the carbonic dioxide of the air until the alcohol began to boil. The excess of ester was washed out of the dry residue with benzol, and the salt dried at 100°, and analysed with the following results:

I. 0.2102 gram of the salt gave after treatment with sulphuric acid 0.0361 gram of sodic sulphate.

II. 0.2056 gram of the salt gave 0.0407 gram of sodic sulphate.

III. 0.2531 gram of the salt gave 0.0390 gram of sodic sulphate.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCNaCO_2C_2H_5$.	Found. I.	II.	III.
Sodium	5.79	5.56	6.41	4.99

It is evident from these results that the method of preparation is unsatisfactory, and we ascribe this to the action of the sodic hydrate (or ethylate) on the bromine, and perhaps also on the acetacetic radical, as, when these two sources of error were removed by using the anilidodinitrobenzylmethylketone, an excellent result was obtained. Bad as these analytical results are, they show that the salt contains but one atom of sodium, and therefore must have the formula which we have ascribed to it.

Properties.—The sodium salt of the bromdinitrophenylacetacetic ester forms a brick-red amorphous mass, easily soluble in water, alcohol, or ether, but insoluble in benzol. Much less freely soluble in a solution of sodic hydrate than in water. Strong nitric acid decomposes it, giving apparently the unaltered ester.

Bromdinitrobenzylmethylketone (*Bromdinitrophenylacetone*), $C_6H_2Br(NO_2)_2CH_2COCH_3$.

This substance can be made from the bromdinitrophenylacetacetic ester by the action of dilute sulphuric acid in open vessels, or of strong hydrochloric acid in sealed tubes. The method of preparation which gave us the best results was as follows: 2 to 2.5 grams of bromdinitrophenylacetacetic ester were boiled with about 200 cc. of sulphuric acid of specific gravity 1.44, boiling point 132°, in a flask with a return condenser, until all the solid was dissolved, which took usually from one hour to an hour and a half. The yellow solution was then allowed to cool, when it deposited a heavy white flocculent precipitate, which was increased in quantity by diluting largely with water; it was filtered out, and after thorough washing with water was purified by crystallisation from alcohol until it showed the constant melting point 112°–113°, when it was dried at 100° for analysis. If the ester used in this process was not perfectly pure, a tarry impurity was formed which could be removed only with great difficulty; the best plan in such a case was to wash the product with a small quantity (20–30 cc.) of benzol, which dissolved the ketone more readily than its impurity, but even after this treatment tedious crystallisation from alcohol was necessary to obtain a pure substance.

The formation of this substance by heating the bromdinitro-

phenylacetacetic ester with hydrochloric acid is not a good method of preparing it, because the process must be carried on in sealed tubes, and also because the product is apt to be contaminated with the tarry impurity just mentioned; but as it throws light on the reaction which takes place, we will describe it briefly: 1 gram to 1.5 gram of the ester was sealed in a tube with 20–30 cc. of pure strong hydrochloric acid, and heated from 130°–150° for two or three hours. Upon opening the tube a gas was evolved which burned with a smoky green-bordered flame (ethylchloride), and also contained carbonic dioxide, as shown by its giving a precipitate with lime-water. The contents of the tubes consisting, in addition to the acid liquid, either of tufts of brownish acicular crystals, or a brown oily semi-solid mass, were poured into a large volume of cold water, and the insoluble portions purified as already described.

The following analyses were made in part with substance prepared by the hydrochloric acid process, and in part with that made with sulphuric acid:

I. 0.2312 gram of the substance gave on combustion 0.3005 gram of carbonic dioxide, and 0.0546 gram of water.

II. 0.1638 gram of the substance gave 14 cc. of nitrogen at a temperature of 23° and a pressure of 755 mm.

III. 0.1862 gram of the substance gave, according to the method of Carius, 0.1173 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCH_3$.	Found. I.	II.	III.
Carbon	35.64	35.44	...	...
Hydrogen	2.31	2.62	...	...
Nitrogen	9.24	...	9.57	...
Bromine	26.40	...	...	26.81

It is evident from the analyses and observations given above that the reaction with hydrochloric acid runs as follows:

$$C_6H_2Br(NO_2)_2CH_2COCHCO_2C_2H_5 + HCl = C_2H_5Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COCH_3;$$

and that the reaction with sulphuric acid must be similar. We had expected that bromdinitrophenylacetic acid would be formed also by these processes, but after a most careful search for it not a trace could be detected; and as its properties are so striking that we could not have overlooked it, the conclusion is forced upon us

that the reaction consisted only in the formation of the ketone. This result is the more remarkable because Heckmann[1] obtained from the orthoparadinitrophenylacetacetic ester by treatment with sulphuric acid of about 10 per cent. exclusively the dinitrophenylacetic acid without a trace of the corresponding ketone. As the presence of bromine in our compound could hardly have caused such a great difference in the action of the sulphuric acid, we infer that it must have been caused by the difference in strength of the sulphuric acid, Heckmann's containing about 10 per cent. of H_2SO_4, while ours contained 54 per cent. This inference will be tested by experiment in the coming year.

Properties.—The bromdinitrobenzylmethylketone crystallises from hot alcohol by cooling in white rectangular plates, often with a right-angled notch in one corner, sometimes also in plates with parallel sides and a deep notch in each end, which makes them look like reels. If crystallised by the evaporation of its alcoholic solution, it forms cylindrical tufts of needles looking like spires of moss, or much branched forms resembling certain seaweeds. Both the plates and the branching needles commonly occur together. It melts at 112°–113° and is essentially insoluble in ligroine; nearly insoluble in cold water, more soluble in hot, but still very sparingly; slightly soluble in ether, carbonic disulphide, benzol, or methyl alcohol, its solubility in the last two solvents is increased by heat; tolerably soluble in ethyl alcohol in the cold, freely when hot; ethyl alcohol dissolves it more freely than methyl alcohol; tolerably soluble in glacial acetic acid; soluble in chloroform; and freely soluble in acetone. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when warmed dissolves it, forming a colorless solution from which water precipitates the ketone essentially unaltered, although it appears at first in spherical groups of thickly set radiating needles, a form in which it is also obtained sometimes when prepared by the action of sulphuric acid on bromdinitrophenylacetacetic ester, but these crystals are converted by crystallisation from alcohol into the rectangular plates described above. Strong nitric acid acts like strong sulphuric acid.

The bromdinitrobenzylmethylketone has well marked acid properties, and in this respect far surpasses the desoxybenzoine from which according to Victor Meyer[2] no sodium compound

[1] Ann. Chem. (Liebig) **220**, 134.

[2] Ber. d. chem. Ges. **21**, 1291 (1888).

could be isolated. In alcoholic solution the ketone gives a dark purplish red color with sodic hydrate or ethylate. Aqueous ammonic hydrate gives only a slight red color with it, which is increased by warming for a short time, and still more by the addition of alcohol, but the color disappears if the heating is long continued. Aqueous potassic carbonate gave no action, but on the addition of alcohol a very dark purplish red solution of the salt. Acid sodic carbonate had no action in aqueous solution, and only very slight on addition of alcohol. The dark red alcoholic solution of the ammonium or sodium salt, if made with an excess of the ketone, is decomposed by water, giving a white precipitate of the ketone. The decomposition is not complete, however, as the liquid retains a pale red color. In the presence of an excess of sodic hydrate, the salt is much more stable. An attempt was made to study the action of the pale red aqueous solution of the ammonium salt with various reagents, but no characteristic precipitates were obtained, probably on account of the small amount of salt left in solution.

We tried also to prepare and analyse the sodium salt, the method being that adopted for the sodium salt of the bromdinitrophenylacetacetic ester; but the results of the analyses came much too high, 9.73 and 8.64 per cent. of sodium, instead of the 7.07 per cent. required by the formula. The reason for this difference is that the sodic hydrate or ethylate removed a portion of the bromine from the ketone, and the benzol, dissolving the organic product, left the sodic bromide formed with the salt of the ketone, as was proved by dissolving the salt in water and acidifying with nitric acid, when, after removing the precipitate by filtration, argentic nitrate gave a heavy precipitate of argentic bromide in the filtrate. We accordingly turned our attention to the anilidoketone, our work on which is described later in this paper. We add here the *properties* of the *sodium salt of bromdinitrobenzylmethylketone.* It is a purplish black amorphous substance, very easily soluble in alcohol, forming a dark claret-red solution, the color of which is so much more purple than that of the salt of the corresponding acetacetic ester that the two substances can be easily distinguished in this way; it is decomposed almost, but not quite, completely by water, and is insoluble in benzol.

The ketone is a decidedly reactive substance. When treated with aniline, it gives aniline bromide and the anilidodinitrobenzyl-

methylketone, which is described later. With phenylhydrazine it appears to form a hydrazone, but at the same time the bromine was removed from the benzol ring, so that the product seemed to be a phenylhydrazidohydrazone. It was free from bromine, and exploded when touched with a hot wire; but as its purification offered considerable difficulties, we did not try to investigate it thoroughly. The ketone seems to react in the same way with hydroxylamine, since in this case also bromine seemed to be removed; but as the product did not have inviting properties, we have not attempted to isolate the oxime. If the ketone is dissolved in chloroform, the solution mixed with bromine, and allowed to stand at ordinary temperatures, hydrobromic acid is given off in considerable quantity, and a new substance melting at least 10° higher than the original is formed, which will be investigated in this laboratory next term. It is a curious fact that, if a solution of the ketone in carbonic disulphide instead of chloroform was treated with bromine, no hydrobromic acid was given off, so far as we could find.

Anilidodinitrobenzylmethylketone,
$C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3$.

This substance is prepared easily by the action of aniline on the bromdinitrobenzylmethylketone. The substances were mixed in the proportion of one molecule of the ketone to two of the base, and the mixture, which had a bright red color, warmed for 15 to 20 minutes on the water-bath. The product was then freed from the aniline bromide and any slight excess of aniline by washing with water to which a little hydrochloric acid was added, the residue, which contained no bromine, purified by crystallisation from hot alcohol till it showed the constant melting point 131°, dried at 100°, and analysed with the following result:

0.1980 gram of the substance gave 23.2 cc. of nitrogen at a temperature of 25° and a pressure of 771.2 mm.

	Calculated for $C_6H_3C_6H_5NH(NO_2)_2CH_2COCH_3$.	Found.
Nitrogen	13.33	13.26

Properties.—The anilidodinitrobenzylmethylketone forms, when crystallised from alcohol, bright yellow groups of curving needles, which look at first like two heads of palm-trees cut off at the point where the leaves grow out of the trunks and put with the stumps

together. As more crystals are formed the groups develop into irregular chestnut-burs. It melts at 131°; is essentially insoluble in ligroine; nearly insoluble in cold water, slightly soluble in hot, forming a pale yellow solution; slightly soluble in ether; soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; soluble in benzol, carbonic disulphide, or glacial acetic acid; freely soluble in chloroform or acetone. Alcohol is the best solvent for obtaining crystals. Strong sulphuric acid dissolves it, forming a brown solution. Strong nitric or hydrochloric acid dissolves it with a yellow color, but it is very slightly soluble in hydrochloric acid.

The acid properties of this substance are much less marked than those of the corresponding bromine compound, as was to be expected from the substitution of bromine by the basic radical C_6H_5NH. Aqueous sodic hydrate has no action on it in the cold, and but slight when warm, but if alcohol is added a brownish red solution of the sodium salt is obtained. Ammonic hydrate, on the other hand, could not be made to act on it, even by warming in presence of a large excess of alcohol. Potassic carbonate in aqueous solution had no action on it, either cold or hot, but gave a very slight action when a large quantity of alcohol was added. The behavior of the solution of a soluble salt with various reagents could not be studied, as the alcoholic solution of the sodium salt was decomposed completely by diluting it with water. But in spite of these weaker acid properties we selected the sodium salt of this substance for analysis, as there was no danger of a decomposition of this ketone by the alkali used, such as had prevented us from getting good results with the corresponding bromine compound. For the same reason the hydrazone for analysis was prepared from this substance instead of from the bromdinitrobenzylmethylketone.

Sodium Salt of Anilidodinitrobenzylmethylketone,
$C_6H_3(C_6H_5NH)(NO_2)_2CHNaCOCH_3$.

This substance was prepared by adding an alcoholic solution of sodic ethylate to an excess of the ketone also dissolved in absolute alcohol. The narrow beaker containing the mixture, after the addition of a little ether, was sunk to its rim in a steam bath. In this way, at first the ether, and later the alcohol vapor, prevented the carbonic dioxide of the air from acting on the salt during the

evaporation. The dry residue was thoroughly washed with benzol to remove the excess of the ketone, and the salt thus purified dried at 100°, and analysed with the following result:

0.2380 gram of the salt gave after evaporation with sulphuric acid 0.0500 gram of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2C_3OH_4Na$.	Found.
Sodium	6.82	6.80

Properties.—A brownish black mass, soluble in alcohol, giving a much browner solution than any of the other salts described in this paper, so that it could be recognised with ease by its color. It is decomposed at once by water, the brown alcoholic solution being turned yellow and turbid. It seems to be nearly or quite insoluble in ether, and is insoluble in benzol.

Anilidodinitrobenzylmethylketonehydrazone,
$C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.

This substance was made by warming for 20–30 minutes on the water-bath in an open dish a mixture of anilidodinitrobenzylmethylketone with phenylhydrazine in the proportion of one molecule of the former to about one and a half of the latter, so as to have a decided excess of the hydrazine. At the end of this time the mixture had changed from yellow to dark carmine red, and solidified to a tarry mass, which was crystallised once or twice from alcohol to bring it into a finely divided state, and washed with water containing a little hydrochloric acid till the excess of phenylhydrazine had been removed, after which it was boiled with alcohol on the water-bath, and while boiling enough benzol added cautiously to effect the solution; the mixture was then boiled for about a minute, when upon cooling crystals were deposited, and this crystallisation was continued until the substance showed the constant melting point 140°, when it was dried at 100°, and analysed with the following result:

0.2177 gram of the substance gave 32.5 cc. of nitrogen at a temperature of 22° and a pressure of 763 mm.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.	Found.
Nitrogen	17.28	16.97

Properties.—The hydrazone crystallises well in reddish brown scales, resembling strongly in general appearance the officinal ferric

citrate. The scales often reach a diameter of 3 to 4 millimeters. Under the microscope plates were observed which seemed to belong to the monoclinic system, but with these were very irregular forms, often serrated on one or both sides, or irregularly diamond-shaped with re-entering angles, usually either grouped in radiating masses, or in crowded branching collections of thick needles. It melts at 140°, but, as it seems to be slightly decomposed by crystallisation, it was difficult to determine the melting point with perfect exactness. It is essentially insoluble in ligroine or cold water; very slightly soluble in boiling water or in ether; slightly soluble in cold alcohol, more soluble, but still not freely, in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold glacial acetic acid, freely in hot; soluble in cold benzol or carbonic disulphide, freely soluble in these solvents when hot; easily soluble in chloroform or acetone, even in the cold. As the benzol solution deposits the substance in a viscous state, it is best to crystallise from a mixture of alcohol and benzol, as described above in speaking of its preparation. Strong hydrochloric acid has no action upon it. Strong nitric acid seems to decompose it, dissolving a little of the product. Strong sulphuric acid dissolves it with a yellowish brown color.

Neither sodic or ammonic hydrate, nor potassic carbonate, nor acid sodic carbonate, gives any action with it in aqueous solution, hot or cold, or even on addition of alcohol; but if it is warmed with sodic hydrate, water, and alcohol, a little dissolves with a brown color, and if a drop of sodic hydrate is added to an alcoholic solution, a dark brownish red solution is formed, which is decomposed by water. It may be, therefore, that the substance has not lost completely the power of forming salts, but it is on the whole more probable that the salt is derived from anilidodinitrobenzylmethylketone formed by the action of the sodic hydrate on the hydrazone, as the action was certainly accompanied by decomposition, since there was a smell of isocyanphenyl, and the hydrazone could not be recovered from the solution in sodic hydrate.

The study of the bromdinitrobenzylmethylketone will be continued in this laboratory.

REVISION OF THE ATOMIC WEIGHT OF GOLD.

By J. W. Mallet, F. R. S.,
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[Continued from page 99.]

Fifth Series of Experiments.

In these experiments an attempt was made to determine the ratio between the weights of metallic gold and metallic silver deposited by the passage of one and the same electric current successively through solutions of the two metals. The simplicity and accuracy with which the direct weighings may be made seemed to present decided advantage, but various difficulties were encountered, and, after the expenditure of a very large amount of time and labour upon the method, it cannot be said, on the whole, to have satisfied me with its results.

While taking due note of the recent literature on the subject of the quantitative electro-deposition of metals from their solutions, especially the reports of work by A. Classen,[1] Lord Rayleigh and Mrs. Sidgwick,[2] Dr. Gore,[3] Thos. Gray,[4] and W. N. Shaw,[5] the author of the present paper made for himself a somewhat extended preliminary examination of the effect of varying conditions on such depositions, so far at least as seemed to be required for his immediate purpose.

The general arrangement of apparatus adopted consisted of a horizontal strip, 4 mm. thick, of vulcanite, or hard vulcanised india-rubber, about 26 cm. long by 3 cm. wide, near each end of which and in the middle of the width were two small holes, through which passed short bits of brass rod, each having attached to it above a binding screw, and below a forceps-like clip, which could be opened by pressure on two little outside studs, but closed firmly, on release of this pressure, by the elasticity of the metal. In these clips were supported the plates of metal to be immersed in the electrolysed solutions, and to serve as anode and cathode terminals respectively, there being two pairs of such plates, one pair near each end of the vulcanite strip, with

[1] A. Classen, Quantitative chemische Analyse durch Electrolyse, 2te Aufl., Berlin, 1886.
[2] Phil. Trans., 1884, 411. [3] Nature, March 16, 1882; Feb. 1 and Feb. 15, 1883.
[4] Phil. Mag., Nov. 1886, 389; and March, 1888, 179. [5] Ibid., Feb. 1887, 138.

four corresponding binding screws. The electric current passed from the first binding screw through one of two metallic solutions—as, for instance, that containing gold—between the first pair of plates, consisting of the same metal as that in this solution, then from the second binding screw to the third (at the other end of the vulcanite strip) by a stout copper wire above, and then through the second of the two solutions—as, for instance, that of silver—between the second pair of plates, consisting again of the same metal as that in the solution in which they were immersed, thus reaching the fourth and last binding screw, the first and last binding screws being, of course, connected by wires with the terminals of the galvanic cells used to develop the current. Fig. 3 shows the disposition in question. The source of the electric

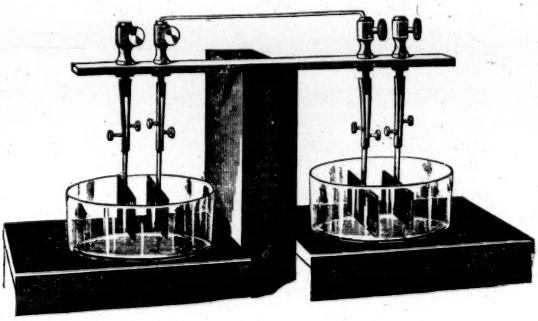

FIG. 3.

current was for the most part galvanic cells of the Meidinger pattern, but in some of the experiments small Daniell cells, and also a Clamond thermo-electric battery, were used. The lower parts of the clips were heavily electroplated with the same metal as that in the solution to which they respectively belonged, in order to avoid any risk of contamination of the solution, in case there should be spattering or accidental immersion, even for a moment, of any part of the clip.

It was decided to place the plates vertically in the liquids, but to make the vertical height small in proportion to width, so as to preserve as far as possible a uniform condition of the solution in

depth. The form adopted for the plates was that of Fig. 4, the shaded part of the surface being coated with hard paraffine, with a view to preventing the strip by which the anode plate was sus-

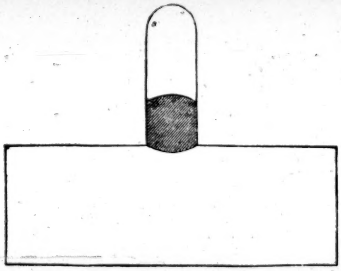

FIG. 4.

pended from its clip being cut across by solvent action at the surface of the liquid. This coating of paraffine was put on after the plates were first weighed, and carefully removed before the second weighing. The four plates for each experiment were of equal size as to length and breadth; in most of the experiments the immersed surface (of one side) measured about 25 square centimeters, though in some cases plates of double this size were used. The thickness was the same for plates of the same metal, but those of the different metals to be compared were made to differ in thickness to such an extent as to allow for the different rate of solution to be expected of the anode plate. I was indebted to the kindness of Mr. Eckfeldt, of the Philadelphia Mint, for having plates of "proof" gold and silver specially rolled for me with all necessary precautions as to perfect cleanliness of the rolls etc., so as to obtain the determinate thicknesses desired.[1]

[1] Mr. Eckfeldt informed me that his method of preparing the proof silver used for these plates was as follows: "Nitrate of silver from the gold assay parting is, after careful filtering, precipitated with hydrochloric acid, and the chloride of silver, after a thorough washing with pure water, is dried and reduced in the melting pot with pure carbonates of soda and potash and carbon in the shape of wheat flour, the melting being done in a clay crucible. The resulting silver bar is then dissolved in dilute nitric acid, and after standing some time filtered, precipitated, and reduced as before; then remelted with the addition of pure nitrate of potash and borax. This generally gives a bar somewhat brittle (crystalline in fracture). It is then remelted, and stirred with a pine stick, and chloride of ammonium added; when the chloride has disappeared the metal is poured. I find this method more satisfactory than any other I have tried."

By heating in a Sprengel vacuum I found traces of oxygen in the rolled silver plates, and extremely minute traces of gas, apparently also oxygen, were likewise obtained from the gold plates, before either had been used.

The middle of the vulcanite strip was supported at a suitable height, so as to allow of equal immersion of the two pairs of plates in their respective solutions, which were contained in small vessels of good hard glass, free from lead. Care was taken to keep the vulcanite strip dry, so that there should be no practical defect of insulation between the two plates of each pair; the necessity for this precaution having been shown in some of the very early preliminary experiments with copper plates, using a wooden supporting strip; some puzzling results being traced back to a little accidental moistening with sulphate of copper solution of the part of the strip between one pair of plates, while those of the other pair were well insulated as to the strip from which they hung.

In all the experiments the two pairs of plates, previously ignited in the Sprengel vacuum, cooled and weighed, were placed in position in the clips, the distance between the parallel surfaces of the plates of each pair being the same, and in most of the experiments measuring about 2.5 cm., and connection was made with the terminals of the galvanic cell or cells used before immersion of the plates in the metallic solutions. All four plates were immersed at the same moment, and at the end of the experiment were in like manner lifted out of the solutions at the same moment, before the current had been broken. They were immediately introduced into one after another of several portions of distilled water before removal from the clips, thorough washing, heating in the Sprengel vacuum, and final weighing.

A preliminary course of experiments was carried out with plates of pure electrotype copper (both pairs) in solutions of cupric sulphate, in order to test the effects, if any, of the following differences in the conditions of the two electrolysis cells compared.

1. *Effect of Difference in the Degree of Concentration of the Two Solutions.*—The solution in one of the two vessels in which the plates were immersed being made to contain but one-tenth the proportion of cupric sulphate existing in the other, acidification and all other conditions being the same for both, only a very minute difference was found between the quantities of copper deposited in the same time on the two cathode plates, and the

difference was not invariably in the same direction. The tendency, however, seemed on the whole to be toward a slightly larger amount thrown down from the stronger than from the weaker solution. In every case there was decidedly more copper dissolved from the anode than was deposited on the cathode plate.

2. *Effect of Difference in Acidity of Two Solutions, otherwise of the Same Strength.*—With the same proportion of cupric sulphate in both solutions, one was made to contain but one-tenth as much free sulphuric acid as the other; all other conditions remained the same for both. As before, the difference of result was insignificant, and somewhat variable in direction, with an apparent tendency towards a very slightly greater deposit on the cathode plate in the less acid as compared with the more acid solution. As before, there was in every case a distinctly greater loss of copper from the anode than gain on the cathode plate, especially in the more acid solution.

3. *Effect of Difference in Temperature of the Two Solutions.*—The proportion of cupric sulphate and of free acid being the same for both solutions, and all other conditions the same, one of the two, however, being maintained at 72°, 47°, or 37° C., while the other was at 2° C., thus establishing a difference in temperature of 70°, 45°, or 35° respectively, there was distinctly in every instance rather more copper thrown down on the cathode plate in the colder than in the warmer solution. The loss of weight of the anode plate was always greater than the gain at the cathode, and the difference in this respect was greater in the warmer than in the colder solution.

4. *Effect of Difference in the Size of the Plates.*—All other conditions being the same in both the electrolysis cells, the plates in one were made to present but one-fourth the surface of those in the other, so that the "current density" was proportionally increased in the former. Under these circumstances there was a constant, though but small, difference in the amount of copper deposited on the two cathodes, the quantity being greater on the cathode plate with smaller surface. The tendency seemed to be towards a greater excess of metal removed from the anode over that deposited on the cathode plate in the case of the larger plates, as compared with the smaller.

5. *Effect of Difference in the Distance between the Plates.*—The plates of both pairs being equal in size, and all other condi-

tions being uniform, the plates in one of the two electrolysis cells were placed at a distance apart only one-fifth that intervening between those of the other pair. It was not clear that any constant difference of result could be detected, but the tendency seemed to be rather toward a very slightly greater deposit on the cathode plate in the case in which the plates were farther apart as compared with that in which they were nearer together. There was no recognisable difference in the proportion of metal dissolved off from the anode plate.

Similar experiments were made with two pairs of plates of pure silver, thus checking the results obtained with copper, and contrasting the behavior of one at least of the less chemically alterable metals with that of the more easily alterable copper. It was intended to make a set of similar experiments also with gold plates only, but the available supply of pure gold in the form of rolled plates was not sufficient for the numerous experiments required. The silver solution used was one of potassium argentocyanide, and the substitute for the free sulphuric acid of the copper experiments was an excess of potassium cyanide. The results obtained were essentially similar to those of the copper experiments, the effect of difference in temperature between the two solutions being, however, less decided, and the slight effect of difference in the size of the plates ("density of current") less constant and distinct.

In all the preceding experiments it was found that the most constant results under otherwise similar conditions were obtained by using feeble currents rather than those of greater strength, especially in the case of the silver solutions. There seemed, however, to be a limit to this. On the whole, the most satisfactory results were obtained (both in these preliminary experiments and in those aiming at the atomic weight determination) with currents not exceeding $\frac{1}{100}$th of an ampère per square centimeter of surface of (one side of) the opposed plates, and in some cases a current but one-fifth of this maximum was used.

Having in view the indications afforded by the preliminary experiments, it was determined to use tolerably strong solutions of the metals to be deposited, with not more than a moderate excess of free acid, or, in the case of the double cyanide solutions, excess of potassium cyanide, to maintain the same temperature in both the electrolysis cells, and to have this temperature as low as

possible (about 2° C.), and to have the plates of the two metals to be compared equal in size, and at equal distances apart, using a weak electric current, and keeping watch over its strength by means of an ordinary hydrogen voltameter in the circuit.

In the actual experiments on the deposition of gold as compared with silver, it was originally proposed to use a solution of potassium auri-cyanide against one of potassium argento-cyanide, with the expectation that 3 atoms of silver would be thrown down for 1 atom of gold. But the first attempts made showed clearly that this reaction could not be obtained. The comparison as to gain in weight of the gold and silver cathode plates gave results leading to an atomic weight for gold impossibly high if the silver deposited were taken to represent 3 atoms, and much too low if it were taken to represent but 1 atom. Hence it appeared that the potassium auri-cyanide had been partially, but not completely, reduced to auro-cyanide by the action of the current, and an intermediate result obtained as to the equivalent quantity of silver between that due to the one or the other gold salt if exclusively present.

A change was therefore made to the auro-cyanide in the preparation of the solution to be electrolysed. A pure form of potassium cyanide was prepared with the aid of alcohol, and carefully tested as to the absence of any metal capable of deposition from the watery solution on electrolysis. Auric chloride was precipitated by ammonia, the fulminating gold, after washing, dissolved in a strong solution of this potassium cyanide with the aid of heat, and the auro-cyanide crystallised out by cooling. The crystals were washed, redissolved in water, aurous cyanide separated from the solution by evaporation with hydrochloric acid, and the crystalline powder after cautious washing again dissolved in potassium cyanide solution, using for the purpose the barely necessary amount of the solvent liquid, but afterwards adding a further quantity, so as to have potassium cyanide in excess. Potassium argento-cyanide was prepared by precipitation of a solution of pure silver in nitric acid with the purified potassium cyanide, washing the precipitate, and re-solution with the aid of the necessary quantity of potassium cyanide, of which finally a moderate excess was added. The solutions of the gold and silver salts were made of equivalent strength, for the most part at the rate of 7 grams of metallic gold for each 100 cc. of solution, and an approx-

imately corresponding amount of silver, taken atom for atom. Both solutions received the same excess of potassium cyanide, generally equal to one-half of that already present in the double salt, but in some of the experiments it was found necessary to add yet more during the electrolysis in order to preserve the purely metallic character of the surface of the plates. As an additional security against admixture of auri-cyanide with the auro-cyanide of the gold solution, it was sub ected for some time to electrolysis with unweighed gold plates immersed, these being reversed two or three times in position, just before the introduction of the weighed plates for a quantitative experiment. A number of attempts were made to substitute for the solution of potassium auro-cyanide one of sodium auro-thiosulphate, of potassium or sodium auri-chloride, and of simple auric chloride, in the last two cases employing at the same time a solution of silver nitrate, but these efforts led to no success.

In many of the experiments made with the double cyanide solutions the cathode plates, both of gold and silver, after removal from the electrolysis cells and thorough washing, were found to curl up on being heated, the deposit, which in these cases was rather hard and brittle, swelling up in a remarkable way, with formation and bursting of little blebs or minute bubbles of the metallic surface, and parting off to some extent of the deposit from the original plate underneath. When the heating was carried out in the Sprengel vacuum small but quite appreciable amounts of hydrogen were found to be given off, having been occluded in the metal deposited. It seemed necessary to throw aside the results in all cases in which this condition of the deposit was well marked. Other experiments were vitiated by the gold deposit not being thoroughly compact, and still others by the surface not being clearly metallic, aurous cyanide making its appearance from the solution. It was hoped that in the experiments, free from apparent defect, any irregular behavior of the gold solution at first might be got rid of by continued electrolysis, with reversal of the anode and cathode plates when necessary, until the ratio of gold to silver deposited should become constant; but confidence in this was greatly shaken when an instance occurred, followed afterwards by others, of sudden change in this ratio, attended with much less loss from the anode gold plate than the gain of the opposed cathode

plate, pointing to deposition of gold from the auro-cyanide with simultaneous formation of auri-cyanide in the solution.[1]

Altogether but five experiments made in this way yielded results which seemed worthy of being used to determine the atomic weight of gold, and it is of course unsatisfactory to know that these were selected out of a much larger number, mainly because, while not known to be in any way vitiated by apparent defects, they lead to values for the atomic weight in question close to those obtained by other methods and other experimenters. It is possible that this near approach to agreement may merely result from a balance of errors in opposite directions, which, taken separately, would have caused the experiments to be rejected. Some other experiments, under apparently similar conditions, gave figures for the atomic weight differing from those reported by one or two whole units.

These only admissible results are the following:

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited, grams.	Silver deposited, grams.
I.	A, *b*.	B	5.2721	2.8849
II.	"	"	6.3088	3.4487
III.	"	"	4.2770	2.3393
IV.	"	"	3.5123	1.9223
V.	"	"	3.6804	2.0132

Aside from other difficulties liable to be encountered in carrying out this electrolytic method, the two most important sources of possible inherent error which suggest themselves are the occlusion of hydrogen by the metallic deposit and the instability of the atomicity of gold in the solution electrolysed.

The separation of hydrogen on the cathode plate, whether in bubbles (which may be avoided by proper regulation of the current) or occluded by the metal (which does not seem to be completely avoidable with any current, although the amount of occluded gas was extremely small in a number of my experiments), must be ascribed to decomposition, simultaneous with

[1] Hittorf (Poggendorff, Annalen, [4], **16**, 523), in the simultaneous electrolysis of gold and silver solutions, the gold as potassium auri-chloride, obtained results which showed that this metal was deposited at the rate of 1 atom for 3 of silver. Calculating on this basis from his two experiments, the atomic weight of gold comes out = 196.311 and 194.197; for silver = 107.66.

In one experiment of my own, using sodium auri-chloride, the result showed that the gold was thrown down for the most part as a triad, but partly as a monad, element.

that of the cyanide of gold, either of water or, more probably, of cyanide of potassium, with secondary action of the potassium on the water. In either case it is by no means clear that the proportion of current giving rise to this liberation of hydrogen can be counted upon as the same in the gold solution and in that of silver, and hence, even though it be fairly assumed that Faraday's principle of equivalent electrolysis by the same current is strictly correct for the *ensemble* of chemical actions in the two cells, the portion of current actually concerned in depositing gold or silver only in each of the respective cells may conceivably not be quite the same, so that the weights of the two metals thrown down may not be strictly equivalent.[1] It was, therefore, deemed important to work with feeble currents, and, while heating all the plates in a Sprengel vacuum before weighing, to reject the results of all those experiments in which the quantity of gas thus discharged amounted to more than the merest trace. But, if the source of error in question still exist at all, it might affect the atomic weight of gold in comparison with that of silver, either by making the former appear higher or lower than the truth.

The source of error most to be feared, however, in connection with the application of this electrolytic method to the determination of the atomic weight of gold, is the uncertainty of having all the gold throughout the process in the form of potassium auro-cyanide in the solution, in view of the transition observed to auri-cyanide during electrolysis, although change in the opposite direction occurs with even greater ease. Each of the two salts appears to admit of electrolytic decomposition, and the presence of any traces of the auri-cyanide, in which the gold has triad character, while the calculation is based on the supposed presence of monad

[1] As bearing on the question of the simultaneous decomposition of two electrolytes in the same solution, the following results may be recorded of an experiment made with a solution of mixed zinc and copper sulphates, with excess of potassium cyanide, the anode plate being of brass and the cathode plate of platinum, and an analysis made of the proportions of the two metals in the anode plate, in the solution as first taken, and in the alloy deposited on the cathode plate and subsequently dissolved off from it by means of nitric acid.

Proportion of copper to zinc.	In the brass anode plate.	In the solution electrolysed.	In the alloy deposited on the cathode plate.
Copper	68.74	13.81	73.34
Zinc	31.26	86.19	26.66
	100.00	100.00	100.00

Different results would undoubtedly have been obtained by substituting some other metal for one of those taken.

gold only, would, of course, tend to make the atomic weight of the metal appear lower than the truth.

Sixth Series of Experiments.

These experiments consisted merely in the further application of electrolysis to the deposition of metallic gold from a solution of potassium auro-cyanide, comparing the weight of the metal thrown down, however, not with the weight of silver, but with the volume of hydrogen gas liberated by the action of the same current, the object being to thus secure, with an assumed knowledge of the

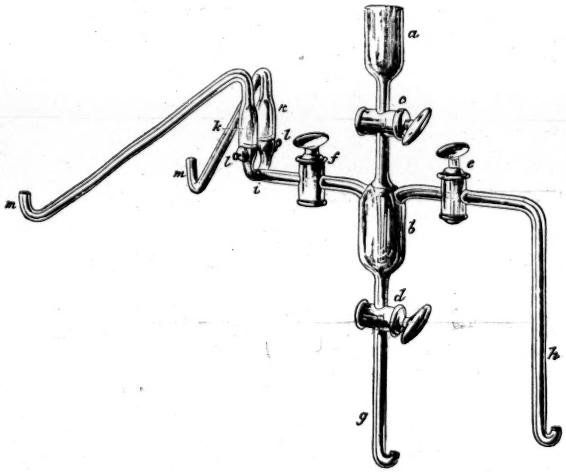

FIG. 5.

density of hydrogen, a direct comparison of the atomic weight of gold with that of the element most generally taken as a basis of the numerical constants in question.

A cell containing the same solution of potassium auro-cyanide as was used in the fifth series of experiments, and having immersed in it a pair of plates of "proof" gold, as already described, was employed for the deposition of the gold. The same current which traversed this cell was passed through a hydrogen voltameter of

special construction,[1] made of glass, in a single piece, the general character of which will be seen from Fig. 5.

When this instrument was to be prepared for use, it was cautiously heated pretty strongly in an air-bath to remove the film of moisture and air from the internal surface, drawing dry air through by means of an aspirator. Clean mercury, previously heated, was then poured in through the funnel *a*, going down to nearly the bottom of the cylindrical vessel *b*, until this vessel—about 30 mm. in diameter and 60 mm. in height—was completely filled, and also the tubes and stopcocks *c*, *d*, *e* and *f*, each of these in succession being opened to allow escape of air, and afterwards closed; *f* was a three-way stopcock, which could either be made to open communication between the parts of the tube on either side of it, or to simply close this tube, or to close this tube and establish communication between the vessel *b* and the outside air through the base of the stopcock; it was in this last-named way that air and surplus mercury were allowed to escape, filling the tube between *b* and *f* with mercury, but not allowing of any of the metal going further along the tube towards *i*. The stopcock *c* was closed, with the tube on which it was situated completely full of mercury, and leaving surplus mercury in the funnel *a*. In filling *b* and its connected tubes care was taken to leave no visible bubbles of air. Pure water mixed with one-twelfth its weight of pure sulphuric acid was boiled for some time in a small flask to expel all dissolved air, keeping up the volume by additions from time to time of water kept boiling in a second flask; the lower turned-up end of the tube *h* was then immersed in the dilute acid, and the lower end of *g* in a cup of mercury; on opening the stopcocks *c* and *d* mercury ran out from *g*, and the dilute acid came in through *h*, filling about half full the cylinder *b*. Closing *d* and *e*, opening *c*, and keeping up a supply of mercury in the funnel *a*, *f* was now turned so as to force out through the base of this stopcock the little mercury in the tube behind it, and fill this tube with the acidulated water. Then *f* was turned so as to allow of this acidulated water being forced on to the bend *i* and into the two little voltameter tubes *k* and *k*, filling these about one-third full. While these tubes were being thus filled the extremities of the delivery tubes *m* and *m* were in communi-

[1] This piece of apparatus—an excellent specimen of skilled glass-blowing—was made, from drawings furnished by me, by Mr. Emil Greiner, of 63 Maiden Lane, New York.

cation with a Sprengel pump, so that they were very nearly exhausted of air. The stopcock *f* having been closed, *e* was opened, and by suitable tilting of the apparatus, and running in of mercury from the funnel *a*, nearly all of the acidulated water from *f* backwards was expelled through the tube *h*. A repetition of the procedure by which the cylinder *b* had been partially filled with acidulated water now served to partially fill it with well-boiled and still hot distilled water to which no acid had been added. The two delivery tubes *m* and *m* were severally detached from the Sprengel pump, after allowing (by a special separate arrangement of tubes with stopcocks) hydrogen to enter one of the two and oxygen the other, and when thus filled the ends of these two tubes were dipped under mercury, and the two platinum wires, *l* and *l*, sealed into the voltameter tubes were connected by the little rings on their outer ends with the terminals of the galvanic cells whence the electric current was to be derived, taking care, of course, to connect to the negative pole the wire of the tube already filled in its upper part with hydrogen, and to the positive pole the wire of the oxygen tube. Viewed from the front, the two voltameter and delivery tubes presented the appearance shown in Fig. 6. The little voltameter tubes *k* and *k* had an external diameter of about 12 mm. and a length of 40 mm. The

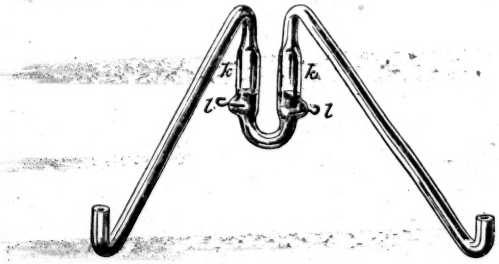

FIG. 6.

platinum wires, *l* and *l*, serving as electrodes were 1 mm. in diameter, and extended beyond the interior surface of the glass (into which they were sealed) for only 3 mm. in length. They could be well covered, and the voltameter tubes filled to one-third their capacity, with only about 2 cm. of the acidulated water.

By careful tilting of the apparatus laterally it was found to be possible to so regulate the pressure of mercury at the ends of the delivery tubes, and therefore the gaseous tension in the two voltameter tubes, that the acidulated water was not forced over from the one to the other, which, had it occurred, would have allowed admixture of the two gases; this required constant watching, however, and there was needed from time to time a little tapping of the apparatus to get rid of the effect of irregular adhesion of the liquid to the walls of the voltameter tubes.

It will be seen that, with the arrangement described, the electrolysis could be effected of acidulated water, thoroughly deprived in advance of dissolved air, and in quantity so small as to be capable of retaining in solution but infinitesimal quantities of the hydrogen and oxygen electrolytically separated. As the decomposition proceeded, the quantity of liquid in the voltameter tubes could be maintained constant by opening the stopcock *c*, with a supply of mercury in the funnel *a*, and then cautiously opening *f*, so as to feed forward a little of the air-free water from the cylinder *b*, thus leaving the proportion of acid unaltered. The surface presented by the platinum wire electrodes was so small as to allow of occlusion of the gases to only an extremely minute extent, and both the hydrogen and oxygen were allowed to escape for some time before any was collected for measurement.

The hydrogen only was collected and measured. I had hoped to apply this form of voltameter to a more exact determination of the relative volumes of hydrogen and oxygen derived from water by electrolysis than is possible with the voltameters of more common construction. But I have not yet seen my way to getting over the difficulties connected with the presence of ozone, hydrogen dioxide, Berthelot's persulphuric acid, or other by-products in the oxygen gas evolved at the positive pole. If this could be accomplished, a useful contribution might possibly be made to the question, revived and worked upon of late by several chemists, of the exact atomic weight of oxygen. The vessel for collecting and measuring the hydrogen, shown in Fig. 7, consisted of a spherical globe of tolerably stout glass, with a capacity of about 250 cm., having a neck of about 1 cm. internal diameter, and 22 cm. long. This neck had etched upon it a simple linear scale of millimeters. At the mouth it was fitted with a well-ground perforated glass stopper, forming part of a glass stopcock with an outer orifice of about 1 mm. bore. The exact capacity of the

whole globe and neck was ascertained by heating it in an air-bath to remove air and moisture condensed on the interior surface, drawing dry air through with an aspirator, then filling the globe with heated mercury, allowing it to cool to an accurately noted temperature, immersing the body of the globe in an outer vessel of mercury so as to prevent extension or flexure of the glass by the weight of the contained metal, filling up to the very mouth with mercury, inserting the stopper with the stopcock open, thus

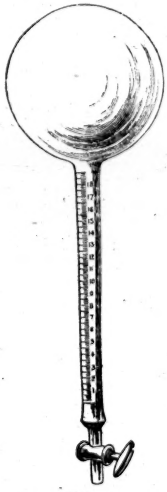

FIG. 7.

forcing out through its orifice the last of the air, closing the stopcock, removing from the orifice tube, by an iron wire, the drop or two of mercury remaining in it, and then emptying the flask and carefully weighing in successive portions the mercury which it had held. The hydrogen from the voltameter was collected in this flask, without its stopper, the flask having been previously filled with mercury, with the needful precautions for removal of all air, and inverted over a mercury trough. In each experiment the process of electrolysis was arrested when the hydrogen had filled the body of the globe and reached to a point rather more than

half way down the length of the neck, the gold plates being of course withdrawn at the same moment from their cell of gold solution, set away to soak in distilled water, and afterwards thoroughly washed, dried, heated in the Sprengel vacuum, cooled, and weighed. The portion of hydrogen collected was dried by successive balls of fused potash introduced and withdrawn by means of platinum wire. The neck of the flask having, in advance of the collection of hydrogen, been passed through a cork, this was used to close the mouth, placed downwards, of a vessel through which a stream of water was caused to flow rapidly from the pipes supplying the University buildings. The atmospheric temperature of the day on which the electrolysis experiment was made having been such as not to differ too much from the temperature of the water from the pipes, the gas occupied such a volume after effectual exposure to this latter temperature that the mercury marked a point somewhere within the length of the neck, which point was noted by the millimeter scale, the thermometer immersed in the flowing water, and the barometer and its attached thermometer being read at the same time. It remained only to insert the stopcock stopper under the mercury of the little mercury trough, close the stopcock, withdraw the flask from the trough, reject the drop or two of mercury from the stopcock orifice by means of a wire, remove the portion of mercury left in the neck of the flask, and weigh it carefully. Its weight, with consideration of its temperature when the stopcock was closed, gave the volume of the portion of the flask not occupied by hydrogen, and, this, subtracted from the whole volume of the interior of the flask, as found by the original calibration, gave the volume, under known conditions of temperature and pressure, of the hydrogen which had been collected. From two calibrations at different temperatures a correction was obtained for the expansion of the glass of the flask, but it was hardly necessary to take this into account, in view of the small limits within which temperature varied in all the experiments made.

But three experiments carried out by this method led to results which seemed worthy of confidence. These results were as follows:

				Hydrogen liberated.	
Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited, grams.	Vol. at 0° C. and 760 mm. cc.	Weight. gram.
I.	A, *b*	C	4.0472	228.64	.02053
II.	A, *b*	C	4.0226	227.03	.02039
III.	A, *b*	C	4.0955	231.55	.02079

In calculating the weight of hydrogen from its observed volume, Regnault's value for the weight of a liter of this gas at 0° C. and 760 mm. was taken as the basis. The correction, of which Lord Rayleigh not long since pointed out the need—namely, for the compression of the vacuous glass flask by atmospheric pressure—was adopted from the experiments of J. M. Crafts (Comptes Rendus, vol. 106, p. 1662); and his corrected value, .08988 gram, was still further corrected for the difference in the force of gravity at Paris and at the University of Virginia (in C. G. S. units, 980.94 : 979.95), giving as the value to be used .08979 gram.

The electrolysis of the water was carried on very slowly, so as to keep the density of the current low with such small electrodes as were used. Nevertheless, as the hydrogen voltameter required constant watching, it became necessary to bring the whole time of an experiment within moderate limits, and hence a considerably stronger current was used than in the simultaneous deposition of gold and silver in the fifth series, this circumstance being less favorable to the satisfactory deposition of the gold. It would have been desirable to use a larger flask and to collect a greater volume of hydrogen; but this, on account of the time required, would have made an experiment exceedingly troublesome and difficult.

In the work of this series the same unsatisfactory need for selecting only such results as came fairly close to the figures expected, and rejecting several others on the ground of very considerable departure therefrom, and the same sources of possible constant error in regard to the gold deposit, present themselves which have already been noticed under the head of the fifth series. As regards the hydrogen, one is led to consider possible diffusion of hydrogen and oxygen between the two little voltameter tubes, and slight imperfection in the drying of the hydrogen obtained. The former would, on the whole, probably tend to diminish the volume of gas collected, and hence to raise the apparent value of the atomic weight of gold. The latter would have the opposite tendency. That neither can have had more than an extremely minute influence was fairly proved by testing a part of the hydrogen obtained, on the one hand by passing it through a red-hot glass tube, and on the other hand by submitting it to more extended drying by contact with phosphorus pentoxide both before and after such heating; in neither case was there appreciable change of volume.

Notwithstanding the desirability of comparing the atomic weight of any other element directly with that of hydrogen, the difficulty is not to be overlooked of doing this for an element having so high an atomic weight as that of gold. There is a manifest objection to the necessity of dealing with such minute quantities of hydrogen as those concerned in these experiments. A very small error in the determination of the hydrogen greatly affects the value found for an atomic weight nearly two hundred times as large. It is true that the measurement of the volume of the hydrogen admits of being made with such precision as to leave room for but an extremely minute error in the corresponding weight, yet this measurement is not one of *limitless* delicacy, particularly if the difficulty be properly appreciated of ascertaining with certainty the precise temperature of the gas at the time its volume is read. Moreover, in measuring the volume of the gas, and thence deducing its weight, there is need not merely for a knowledge of changes of temperature and pressure, but for *absolutely* correct readings of the barometer and thermometer, so that there must usually be a degree of hesitation in accepting the readings of even fairly standard instruments, when temperature and pressure come to be placed in comparison with these conditions as affecting the results of Regnault for gaseous density. Nor can the results of that great physicist be assumed as themselves free from all possible need of further correction.

The error of direct comparison with so small an atomic weight as that of hydrogen is, however, after all only *masked* by substituting an *indirect* comparison through some larger atomic weight, since the assumed value of the latter is uncertain within limits which depend upon *its* comparison with the atomic weight of hydrogen.

Seventh Series of Experiments.

In pursuance of the attempt to connect directly the atomic weight of gold with that of hydrogen, metallic zinc was prepared as nearly as possible in a state of purity, and, a known quantity of the metal having been dissolved in dilute sulphuric acid, the amount of hydrogen evolved was determined by volume. A solution of pure auric chloride or bromide was then treated with a known quantity of the same zinc, more than sufficient for the complete precipitation of all the gold present; the excess of zinc

was dissolved by dilute sulphuric acid, and the volume of hydrogen given off was determined. The precipitated gold was carefully collected, washed, dried, ignited, and weighed. The difference between the volume of hydrogen which the zinc gave when thus partly used to replace a known quantity of gold and the volume which it would have given if replacing hydrogen alone represented, of course, the volume of a quantity of hydrogen equivalent to the gold precipitated and weighed. From this volume, under known conditions of temperature and pressure, the weight of the hydrogen was calculated on the basis of Regnault's results for the density of the gas, after application of the needful corrections, as in the sixth series of these experiments.

In a preliminary notice of my work read before the Chemical Section of the British Association at the Manchester meeting of 1887, it was pointed out that the method just described has certain advantages in principle. It does not require that the weight of the gold salt in solution be known, so that all difficulties in regard to drying such salt without decomposition are disposed of. It does not depend upon a knowledge of the atomic weight of the halogen in combination with gold, or upon a knowledge of the atomic weight of zinc. It does not even require that the zinc be of assured purity, provided only it be uniform in character, so that a given weight of it can be trusted to yield always the same quantity of hydrogen, and there be no impurities present capable of interfering with the collection of the whole of the precipitated metallic gold in a state of purity. The chief difficulty consists in the accurate ascertainment of the total volume of hydrogen evolved from the solution of a satisfactorily large quantity of zinc; when the gold solution comes to be used, as the volume of hydrogen given off on solution of the *surplus* zinc may be made quite small, its measurement becomes both easy and exact.

The pure zinc required was obtained by fractionally distilling in a Sprengel vacuum some very nearly pure metal from the Bertha Zinc Works, in Southwestern Virginia, using a long combustion-tube of hard Bohemian glass, and substantially the same arrangement of apparatus as that described by Morse and Burton[1] in connection with their work on the atomic weight of zinc. The original metal was found, by an analysis in the laboratory of the

[1] This Journal **10**, 312. Tubes of glazed porcelain, closed at one end, had been specially procured for use in thus distilling zinc, but it was found that they were quite unnecessary.

University of Virginia, to contain less than .04 per cent. of foreign matter, almost solely consisting of lead and iron. It was four or five times redistilled *in vacuo*, rejecting each time about one-third of the quantity treated. The process is easily carried out, and in the final product, completely soluble in dilute sulphuric acid without visible residue, no trace of detectable impurity could be found.

For the evolution of hydrogen on solution of this zinc in acid the little piece of apparatus represented in Fig. 8 was used, the same that I had used in my work of several years ago on the atomic weight of aluminum.[1] The description formerly given of the details of an experiment with this apparatus may be repeated with but trifling change of language. A rather more than sufficient

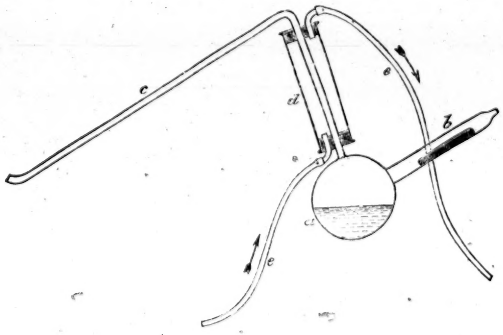

FIG. 8.

quantity of diluted sulphuric acid, its volume accurately measured, having been introduced into the bulb *a* by means of a little tube-funnel, passed through the tube *b*, the outer end of which was originally open, taking care to leave the surface of *b* clean, the metallic zinc, in a single piece of elongated shape, and having a little bit of slender platinum wire wrapped round it, was passed into *b*, held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 mm. from it; *b* was now drawn off in the lamp flame, and sealed with a well-rounded end. The bulb was

[1] Phil. Trans. 1880, 1026.

touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube *c* was introduced into the mercury of the trough, taking care that *b* was still kept in such a position as to prevent the zinc coming in contact with the dilute acid. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in *c* were read off;[1] so that, knowing the volume of dilute acid introduced and of metallic zinc (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to determine the volume of air which the apparatus contained at the beginning. The piece of zinc was now made to slide down into the bulb, the end of the gas delivery-tube *c* having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of zinc rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a rapid current of ice-water was kept up through *d*.

As soon as the last of the zinc had disappeared, leaving the liquid quite clear, *c* was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer and the height of the mercury in *c* above that in the trough were now read and recorded.

Lifting *c* straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in *a*, *b*, and *c* was filled up with solution of zinc sulphate and free acid of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube-funnel, and the volume used noted, so as to show how much liquid had been already present.

The apparatus having been now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference

[1] All readings were, of course, made from a distance with the aid of a small telescope.

between the total capacity (to the level of the mercury in *c*) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

The dilute acid was saturated with pure hydrogen just before being used (and in the experiments with auric chloride or bromide the main portion of water holding this salt in solution was similarly treated), and a preliminary experiment showed that there was but an extremely minute difference between the amount of gas removable from such liquid by heating in a Sprengel vacuum and from that containing zinc sulphate after the solution of the metal; so that, practically, the question of retention of gas in solution by the liquid might be neglected.

The sulphuric acid was diluted to 25 per cent. by weight, only a small bit of platinum wire was wrapped round the zinc, and the temperature of the bulb was not allowed to rise beyond about 20° C. Thus the risk of evolving other gaseous products than hydrogen[1]—as hydrogen sulphide or sulphur dioxide—was avoided, and on testing for these impurities the hydrogen collected no traces of them were found.

The measuring flask used to collect the hydrogen was of the same character as that used for the experiments of the sixth series, but of much larger size, holding about a liter. The quantity of zinc taken for each experiment was calculated to give a volume of gas which, under the conditions of temperature and pressure of the day, would bring the mercury to somewhere near the middle of the neck, and the gas, previously dried by balls of fused potash, was measured after the temperature had been rendered as nearly as possible fixed by the circulation round the outside of the flask of an active stream of water from the laboratory supply pipes. On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than that of the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the gas collected in the flask.

In the experiments with auric chloride or bromide the quantity of hydrogen given off on solution of the *surplus* zinc was so small that it could be easily measured in a little glass tube, the same

[1] Muir and Adie, "On the Interaction of Zinc and Sulphuric Acid," Chem. Soc. Jour. 1888, p. 47.

method of double calibration with mercury being used as for the larger volumes. In these experiments the bulb used had a second side tube, *f*, as shown in Fig. 9, to hold the sulphuric acid, while *a*

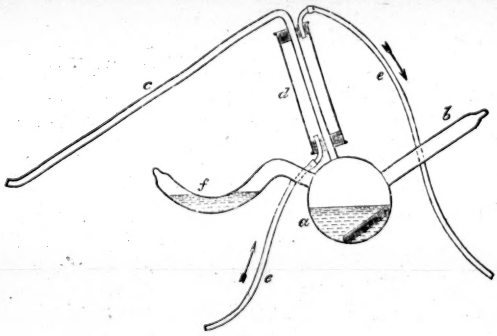

FIG. 9.

contained the aqueous solution of the gold salt; this acid was already somewhat diluted, and was introduced into *a*, after complete precipitation of the gold, very gradually, so as to avoid any considerable rise of temperature. The quantity of water used was such as to make the whole volume of liquid very nearly the same in the experiments with zinc alone and in those with zinc and the auric salt. Care was taken to ascertain, after measurement of the hydrogen, that it had been effectually freed by the potash balls not only from moisture, but from any traces of hydrochloric acid formed and carried over.

In order to connect the weight of the zinc with that of the hydrogen produced by its solution, it was necessary that the weight of the metal should be *absolute*, or in terms of equal value with those used in Regnault's researches on the density of hydrogen; hence, as has been already stated, the weights used were such as had had their real values determined, and the precaution of double weighing was applied. The quantities of metal used being small, the center of gravity of the balance beam was so adjusted as to give great sensitiveness. In calculating the weight of the hydrogen from its volume, the same value for the weight of a liter of the gas

was assumed as has been already stated, viz., .08979 gram, being the result of Regnault's determinations, with the correction pointed out by Lord Rayleigh and numerically estimated by Crafts, and further corrected for the force of gravity at the University of Virginia.

The haloid salts of gold were prepared as for the experiments of the first and second series, and the careful filtration of their solutions was followed by long continued standing at rest before the portions required were gently drawn off for use. Great care was taken in removing the last traces of precipitated gold from the bulb—to facilitate which the connected tubes were all cut off short—and in repeatedly washing the metal, first with dilute sulphuric acid, and then with pure hydrochloric acid, and, finally, with water, before drying, heating (in the Sprengel vacuum), cooling, and weighing.

The results obtained by this method were much freer from irregularity, and much more satisfactory, than those of the electrolytic experiments. All are reported, except one or two cases obviously vitiated by mechanical defects of manipulation, and, in consequence, not carried out to the end.

Experiments with Zinc alone.

Experiment.	Zinc dissolved. grams.	Hydrogen obtained at 0° C. and 760 mm. cc.		Hydrogen, at 0° C. and 760 mm. for 1 gram of zinc. cc.
I.	2.6990	922.64		341.85
II.	2.6771	915.33	Equivalent	341.91
III.	2.7029	924.20	to	341.93
IV.	2.7117	927.51		342.04

Or a total amount of 10.7907 grams of zinc gave 3689.68 cc. of gas,[1] equivalent to 341.93 cc. of hydrogen for 1 gram of zinc. This value was adopted in calculating the fifth column of the following table.

[1] These figures represent an atomic weight for zinc = 65.142, taking the weight of a liter of hydrogen at 0° C. and 760 mm. as .08979 gram, and assuming the zinc used to have been absolutely pure, and the quantity of hydrogen collected to have been strictly equivalent to it; neither of the two latter assumptions is essential to the use made in this paper of the experiments. Reynolds and Ramsay in their recent paper (Chem. Soc. Jour., Dec. 1887, p. 854) on the atomic weight of zinc arrive at a somewhat higher value, on the basis of a like comparison of the weight of the metal with the volume of hydrogen liberated by it, but they assume the weight of the liter of hydrogen under normal temperature and pressure as .0896 gram, which must be considered too low in view of the recently applied correction of Lord Rayleigh.

Experiments with Gold Salt and Zinc.

Experiment.	Character of gold used.	Character of gold salt.	Gold precipitated, grams.	Hydrogen, at 0° C. and 760 mm. Corresponding to total zinc. cc.	Hydrogen, at 0° C. and 760 mm. Obtained from residual zinc. cc.	Hydrogen equivalent to gold. Vol. at 0° C. and 760 mm. cc.	Hydrogen equivalent to gold. Weight, gram.
I.	A, *b*	$AuCl_3$	10.3512	1779.44	—23.34	=1756.10	=.15768
II.	A, *b*	$AuBr_3$	8.2525	1428.99	—28.61	=1400.38	=.12574
III.	A, *b*	$AuCl_3$	8.1004	1393.43	—18.56	=1374.87	=.12345
IV.	C	$AuCl_3$	3.2913	582.82	—24.18	= 558.64	=.05016
V.	C	$AuBr_3$	3.4835	606.20	—15.27	= 590.93	=.05306
VI.	D	$AuBr_3$	3.6421	643.31	—25.20	= 618.11	=.05550

In considering possible causes of constant error in the experiments of this last series it seems most likely that they would affect the exact determination of the weight of the precipitated gold, either by mechanical loss of some minute particles of the metal, tending to lower the atomic weight, or by incomplete washing out of the zinc salt, with an influence in the opposite direction. Any failure to remove the last traces of moisture from the hydrogen was, I think, effectually guarded against, at any rate within such limits as would have sensibly affected the resulting atomic weight; and any error due to retention of hydrogen in solution by the liquid must also have been inappreciably small, in view of the precautions taken and the close similarity of conditions in the experiments with zinc alone and with zinc and the auric salt.

Calculation of Results.

In calculating the atomic weight of gold from the data furnished by the experiments which have been described, I have thought it best to conform to the most general usage of those who have been working on questions of this sort of late years, so as to facilitate comparisons with the results of others. Hence, although the atomic weight has been calculated separately from the figures of each experiment reported, the value deduced from each series has not been taken as the arithmetical mean of the separate results, nor has the probable error of these or of the mean been calculated by the method of least squares, as was done in my paper on the atomic weight of aluminum, but, instead, the general result for each series has been obtained, as in the calculations of Meyer and Seubert, from the aggregate quantities of the materials employed,

though I am by no means convinced that this mode of reckoning is in all cases sound in principle, giving, as it does, weight to each experiment in proportion to the quantity of material employed.

The atomic weight assumed for the other elements involved are those which have been most generally accepted in calculations of this kind, based for the most part on the experiments of Stas, and representing, with greatest probability, the values as at present known to us. They are as follows:

$$H = 1.$$
$$Ag = 107.66.$$
$$Cl = 35.37.$$
$$N = 14.01.$$
$$C = 11.97.$$

Calculated Results.

The following are the values obtained for the atomic weight of gold from the different series of experiments:

First Series ($Ag_2 : Au :: 322.98 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	12.4875	7.6075	196.762
II.	13.8280	8.4212	196.694
III.	11.3973	6.9407	196.688 Lowest value
IV.	5.5286	3.3682	196.770 Highest value
V.	4.6371	2.8244	196.723
	47.8785	29.1620	196.722

Second Series ($Ag_2 : Au :: 322.98 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	13.5149	8.2345	196.789
II.	12.6251	7.6901	196.731 Lowest value
III.	17.2666	10.5233	196.843 Highest value
IV.	4.5141	2.7498	196.746
V.	5.8471	3.5620	196.756
VI.	6.4129	3.9081	196.828
	60.1807	36.6678	196.790

Third Series ($Ag_4 : Au ; : 430.64 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.	
I.	12.4851	5.7048	196.772	
II.	17.4193	7.9612	196.817	Highest value
III.	5.3513	2.4455	196.799	
IV.	9.1153	4.1632	196.685	Lowest value
	44.3710	20.2747	196.775	

Fourth Series ($N(CH_3)_3HCl_4 : Au : : 201.40 : x$).

Experiment.	Loss by ignition of trimethyl-ammonium auri-chloride, grams.	Gold, grams.	Atomic weight of gold.	
I.	7.5318	7.3754	197.218	
II.	7.8432	7.6831	197.289	Highest value
III.	5.2811	5.1712	197.209	
IV.	3.3309	3.2603	197.131	Lowest value
V.	2.8165	2.7579	197.210	
	26.8035	26.2479	197.225	

Fifth Series ($Ag : Au : : 107.66 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.	
I.	2.8849	5.2721	196.747	
II.	3.4487	6.3088	196.945	Highest value
III.	2.3393	4.2770	196.837	
IV.	1.9223	3.5123	196.709	Lowest value
V.	2.0132	3.6804	196.817	
	12.6084	23.0506	196.823	

Sixth Series ($H : Au : : 1 : x$).

Experiment.	Hydrogen, grams.	Gold, grams.	Atomic weight of gold.	
I.	.02053	4.0472	197.136	
II.	.02039	4.0226	197.283	Highest value
III.	.02079	4.0955	196.994	Lowest value
	.06171	12.1653	197.137	

Seventh Series ($H_3 : Au : : 3 : x$).

Experiment.	Hydrogen, grams.	Gold, grams.	Atomic weight of gold.	
I.	.15768	10.3512	196.941	
II.	.12574	8.2525	196.894	
III.	.12345	8.1004	196.851	
IV.	.05016	3.2913	196.848	Lowest value
V.	.05306	3.4835	196.956	Highest value
VI.	.05550	3.6421	196.865	
	.56559	37.1210	196.897	

General Mean of Results.

If each of the foregoing series of experiments be represented by the result calculated from the aggregates of material used, and if equal weight be attached to the results of all the methods, the general mean derived from the whole of the 34 experiments will be as follows:

First series, ...	196.722	Lowest value
Second series, ...	196.790	
Third series, ...	196.775	
Fourth series, ...	197.225	Highest value
Fifth series, ...	196.823	
Sixth series, ...	197.137	
Seventh series, ...	196.897	
General mean, . . .	196.910	

The results of the fifth and sixth series, obtained by electrolysis, are, I am convinced, much less entitled to confidence than any of the others. If these two be excluded, the general mean of the remaining series will be 196.882, a number differing but little from the mean of all.

The highest value is that derived from the fourth series—ignition of trimethyl-ammonium auri-chloride. It has been seen that the individual results of this series agree fairly well with one another, and, when examined in connection with the facts as to the different crops of crystals of the salt used, do not seem to present any evidence of want of uniformity in the material. But, as it may still be suspected that traces of dimethyl- or of monomethyl-ammonium auri-chloride may have been present, and have caused the apparent value of the atomic weight of gold to come out higher than the truth, if we exclude also this series, the general mean of the remaining four will be 196.796.

Finally, if for the sake of comparison with the results of Krüss, and of Thorpe and Laurie, the general mean be taken for the first three series only, in which auric chloride and bromide were examined, the result is 196.762—intermediate between the general means of the two previous researches, but rather nearer to that derived from the work of Thorpe and Laurie than of Krüss.

It will be observed that, although there is pretty close agreement among the means of results obtained by altogether different

methods, this agreement is not so close as that presented by the results of the nearly similar methods pursued in the first three series. This cannot but suggest the probability of there being still sources of minute errors inherent in the methods themselves, and not dependent upon mere imperfections of manipulation in carrying these methods out. Although there is thus to be noticed a slight tendency on the part of each method to yield high or low figures severally, with the exception of the results of the fourth series there does not appear to be any considerable reason to see in the values obtained confirmation of the special suspicions in connection with each method which have been stated. There is no clear evidence of any difference in the results which can be traced to the history of the particular samples of gold used; a larger number of somewhat low results seem to have been yielded by the metal designated as (C)—*i. e.*, obtained from the United States Assay Office at New York—than by the others, but the difference is not marked or constant enough to warrant any trustworthy conclusions as to the character of this material.

Concluding Remarks.

The atomic weight of gold as deduced from the experiments reported in this paper is entirely in accord with the place occupied by the metal in Mendelejeff's "periodic" classification of the elements, but this is equally true of the slightly different values obtained by Krüss, and by Thorpe and Laurie, and the only difficulty at one time apparent as to this point—namely, the relative positions of gold on the one hand and of platinum, iridium, and osmium on the other—has been removed, not by any change in the atomic weight of gold, but by changes affecting the values to be assigned the three other metals, as these values have been determined by Seubert.[1] It is very desirable that, in order to a fuller and more exact examination of the Mendelejeff table of the elements, there be accomplished as soon as possible a general revision of the atomic weights of *all* the elements of well determined individuality, so many of which are still very imperfectly known.

As to any bearing of the results of the present paper on the

[1] Ber. d. chem. Ges. **11**, 1770; **14**, 868; **21**, 1839.

so-called hypothesis of Prout,[1] the general mean of all my results, or even the general mean with exclusion of the values obtained by electrolysis, approaches the integer number 197 rather more nearly than does the final number arrived at by Thorpe and Laurie, and still more nearly than does that considered by Krüss to express the final result of his experiments. If the results of the fourth series be also rejected, my general mean will be nearer the integer than is the Krüss number, but not quite so near as that of Thorpe and Laurie. I feel that somewhat greater confidence may be placed in my own work, simply on the ground of its involving the use of more completely different and independent methods—a principle which I believe to be of the first importance in any attempts at increased accuracy in the determination of atomic weights.

At the same time, as has already been pointed out, this work seems to me to furnish some probable evidence that not all inherent defects of method have been eliminated. Whether or not such defects may exist to an extent sufficient to account for the remaining difference between the value obtained and the integer multiple of the atomic weight of hydrogen there does not seem to be ground on which to express a positive opinion. But this research does not supply any clear evidence contradictory of such a possibility.

On this point, and generally on the attainment of what is sometimes rather too easily spoken of as the greatest possible accuracy in the determination of an atomic weight—particularly of an element for which the value is as high as that for gold—any one who actually works in a conscientious way at such determinations will be pretty sure to feel more strongly the difficulty of the task, and to express himself with more caution, than do some compilers of results in assuming at any time that the last word has been spoken.

[1] Soon after the publication of my paper on the atomic weight of aluminum, I was criticised by a writer of abstracts for the German Chemical Society on account of my use of the expression "Prout's law," amazement being indicated that I should have called the "hypothesis" of Prout a law. If this writer had noticed my use of inverted commas, and still more what was said in the course of two or three pages of the paper, he would have seen that the use of the expression "Prout's law" was by no means equivalent to assuming this to be "a law of nature."

THE ELECTROLYTIC METHOD AS APPLIED TO PALLADIUM.

By Edgar F. Smith and Harry F. Keller.

Our knowledge bearing upon the behavior of this metal towards the current is limited and rather indefinite. In 1868 Wöhler published, in the Annalen, 143, 375, an article entitled "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken: palladium, as the positive pole of a battery consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like color. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. At the same time black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of Classen's Quantitative Electrolysis, p. 72 (Am. edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated[1] that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-colored deposit, which, as it grew more dense, became darker, and finally black in color. At the positive pole there was a simultaneous deposition of oxide, showing a reddish color. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potassium cyanide. In such solution a current, generating 1 cc. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in color, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide

[1] Berg- und Hüttenmännische Zeitung **38**, 121; also Zeit. für anal. Chem. **22**, 240.

solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladious chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black in color. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

The next attempt was made with palladammonium chloride, $Pd(NH_3)_2Cl_2$, in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 cc.; the acting current gave 0.9 cc. OH gas per minute. The poles were distant from each other about two inches. Just as soon as the circuit was completed, a yellowish brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in color made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black color, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behavior is similar to that of nickel when its ammoniacal solutions are electrolysed. In subsequent experiments the course was somewhat modified. From solutions such as just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0.1–0.3 gram. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

Experiment I.—A quantity of palladammonium chloride (= 0.2228 gram Pd) was dissolved in ammonium hydroxide; to this solution were added 20–30 cc. of the same reagent (sp. gr. 0.935) and 75 cc. water. The current allowed to act upon this ammoniacal liquid gave 0.9 cc. oxyhydrogen gas per minute. The

decomposition continued through the night. At no time was there any oxide deposition upon the anode. The palladium gradually assumed a bright metallic appearance. After drying the deposit showed about the same appearance as is ordinarily observed with this metal in sheet form. The washing was limited to hot water, and when the deposit was perfectly dry, the dish containing it was covered with a watch-glass and exposed to a temperature ranging from 110°-115° C. This was done to expel any hydrogen that might possibly have been retained by the palladium.

Weight of silvered dish + Pd = 61.9575 grams.
" " " − Pd = 61.7350

0.2225 Pd.

Experiment II.—In every respect similar to Experiment I, gave

Weight of silvered dish + Pd = 71.9540 grams.
" " " − Pd = 71.7315

0.2225 Pd.

The filtrates from these deposits were warmed for eight hours with ammonium sulphide without showing any formation whatever of palladium sulphide.

In several experiments, with conditions unlike those just described and where consequently an incomplete precipitation of metal occurred, the digestion with ammonium sulphide produced in every instance, in a very short time, a reddish brown flocculent sulphide, carrying with it quite a considerable quantity of free sulphur.

In a second series of two experiments, in each of which there was the same amount of palladium as in the previous trials, the quantity of ammonium hydroxide in excess was made 30 cc., while the current (giving 0.8 cc. oxyhydrogen gas per minute) was allowed to act for sixteen hours. The results were quite concordant:

Experiment III.—Weight of silvered dish + Pd = 72.1055
" " " " − Pd = 71.8825

Weight Pd = 0.2230 gram.

Experiment IV.—Weight of silvered dish + Pd = 62.0512
" " " " − Pd = 61.8280

Weight Pd = 0.2232

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolysed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0.70 cc. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows:

Experiment V.—Weight of silvered dish + Pd = 72.3555
" " " " — Pd = 71.9100
Weight Pd = 0.4455

Experiment VI.—Weight of silvered dish + Pd = 62.2600
" " " " — Pd = 61.8138
Weight Pd = 0.4462

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V, with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method the results may be tabulated as follows:

	Found Pd.	Calculated Pd.
Experiment I.	0.2225	0.2228
" II.	0.2225	"
" III.	0.2230	"
" IV.	0.2232	"
" V.	0.4455	0.4456
" VI.	0.4462	"

If the percentage differences be calculated it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behavior of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form.

UNIVERSITY OF PENNSYLVANIA, *February* 12, 1890.

Contributions from the Chemical Laboratory of the Department of Agriculture.

XV.—ORGANIC ACIDS IN THE JUICES OF THE SORGHUM CANE.

BY H. W. WILEY AND W. MAXWELL.

Preliminary investigations with the juices of the sorghum cane have indicated the presence of the following acids, which have been obtained as free crystallised bodies, or as salts:

A. Volatile	1. Formic acid.		
	2. Acetic "		
B. Oleics	3. Prismatic crystals.	}	Undetermined.
	4. Needle "		
C. Other acids	5. Oxalic acid.		
	6. Tartaric "		
	7. Citric "		
	8. Malic "		
	9. Aconitic[1] "		

These preliminary examinations indicate that the given acids are present in the following order by proportion:

Aconitic, citric, malic, oleic, formic, with decreasing amounts of the others, terminating with mere traces of oxalic and acetic acids.

For want of material the researches will stand over until next season for completion.

[1] See Parsons, this Journal **4**, on Aconitic Acid in Sorghum.

NOTES.

Ethylene-lactic Acid.

In the work of Wislicenus in 1868 and that of Erlenmeyer in 1875, the existence of three lactic acids was definitely proved, and their properties and modes of formation studied. Two ethylidene-lactic acids or α-hydroxypropionic acids, of the structure $CH_3-CH<^{OH}_{COOH}$, and one ethylene-lactic acid, the hydracrylic acid, or β-hydroxypropionic acid, of the structure $CH_2<^{OH}_{CH_2-COOH}$. The differences between the optically inactive ethylidene-lactic acid and the optically active modification—sarcolactic acid—are those we should expect if we accept the hypothesis of Van't Hoff and Le Bel, of physical isomerism due to the presence of an asymmetric carbon atom. Our received theories then account for the existence of these three lactic acids and no more; but Wislicenus isolated from the mother-liquors of zinc sarcolactate a zinc salt, which he supposed to be the salt of an ethylene-lactic acid; he proved that it was not a salt of hydracrylic acid. He could not isolate the ethylene-lactic acid, nor indeed force the syrupy zinc salt to crystallise, but he made and analysed a sodium salt. Mention of this fourth supposed lactic acid found its way into the text-books, and until now this has been one of the doubtful points in chemistry.

Max Siegfried, of the Physiological Institute in Leipsic, publishes a paper in No. 14, Vol. 22, of the Berichte der deutschen chemischen Gesellschaft for 1889 which satisfactorily explains the formation and reactions of this zinc salt.

By extracting with alcohol the mother-liquors of the zinc sarcolactate from one hundred pounds of horse-flesh, the author obtained a syrupy zinc salt having the properties described by Wislicenus; it was not found possible to crystallise the zinc or calcium salt, but crystallised sodium and silver salts were obtained and analysed. The percentage of sodium and of silver was not that of lactates, but by substituting the value of hydrogen for that of silver, in the figures, the formula $(CH_3O)_n$ results. It was observed that the zinc salt when precipitated by ether from its alcoholic solution was not completely soluble in water; Siegfried thought it possible to obtain the free acid from this insoluble portion, and after some difficulty he succeeded in isolating from it an acid crystallising in needles, and fusing at 166°–167°, which he analysed and found to be acetyl-lactic acid,

$$CH_3-CH<^{O(C_2H_3O)}_{COOH},$$

identical with an acetyl-lactic acid made by Wislicenus from a derivative of inactive ethylidene-lactic acid. The author shows

that this acid and its salts are unstable and break down readily in presence of water into acetic and lactic acids,

$$CH_3-CH\begin{matrix}<^{OOC_2H_3}_{COOH}\end{matrix} + HOH =$$

$$CH_3-CH\begin{matrix}<^{OH}_{COOH}\end{matrix} + CH_3-COOH.$$

This behavior explains the figures obtained in the analyses of the salts. Wislicenus found 24.2 per cent. sodium in his sodium salt, and this is the exact figure demanded for a mixture of equal parts of sodium acetate and lactate. The author's figures for sodium varied from 25.74 to 25.81; values lying between those for sodium lactate and acetate. The author's analysis of the silver salt led to the assumption of an acid $(CH_2O)_n$, a formula common to both acetic and lactic acids.

But why should zinc acetyl-lactate be stable when the sodium and silver salts are so readily decomposed? The answer lies in the curious fact that by the action of zinc acetate on zinc sarcolactate in aqueous solution, zinc acetyl-lactate is invariably formed, and the presence of very little of this substance prevents zinc lactate and zinc acetate from crystallising. The zinc salt found by Wislicenus then was zinc acetyl-lactate, not zinc lactate, and with this falls all evidence of the existence of a fourth lactic acid.

In the liquids extracted from meat acetic acid is always present, hence the formation of the zinc acetyl-lactate is clear.

The author has made the acetyl-lactic acid synthetically from zinc lactate and zinc acetate. Solutions of acetyl-lactic acid and of its zinc salt are optically inactive, and on saponification of the acetyl-lactic acid, a salt of inactive ethylidene-lactic acid is formed. On taking up the acetyl group, then, the ethylidene-lactic acid changes from the active to the inactive modification. It may be inferred, then, that inactive ethylidene-lactic acid could be substituted for the active modification in the synthesis of acetyl-lactic acid, and Siegfried finds this to be the case; the products in both instances are identical. E. R.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., *Feb.* 6, 1890.

Editor CHEMICAL JOURNAL:

I beg the favor of calling attention to the fact that the formula given for calycanthine on page 566 of No. 8, Vol. XI, AMERICAN CHEMICAL JOURNAL, is incorrect. The analytical data were sent to me at Toronto last year during the meeting of the American Association, and a mistake of a 7 for a 4 is the cause of the error.

An extensive study of this body with some associated alkaloids is now going on and the full data of the work will be sent to you in due time. H. W. WILEY.